Impact of mangroves and an agriculture-dominated hinterland on the carbon and nutrient biogeochemistry in the Segara Anakan Lagoon, Java, Indonesia

PhD thesis

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Vorgelegt dem Fachbereich 2 (Biologie/Chemie) der Universität Bremen als Dissertation zur Erlangung eines Doktorgrades der Naturwissenschaften

- Dr. rer. nat -

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Calvin: I think we've got enough information now, don't you?

Hobbes: All we have is one "fact" you made up.

Calvin: That's plenty. By the time we add an introduction, a few illustrations, and a conclusion, it will look like a graduate thesis.

(Bill Watterson's *Calvin and Hobbes*)

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I. Honesty declaration/ Eigenständigkeitserklärung

Corr. § 6(5) Nr. 1-3 PromO I herewith declare that I

1) have completed this dissertation unassisted.
2) did not use more than the stated sources and aid.
3) have cited all references.

Gem. § 6(5) Nr. 1-3 PromO erkläre ich hiermit, dass ich

1) die Arbeit ohne fremde Hilfe angefertigt habe.
2) keine anderen, als die von mir angegebenen Quellen und Hilfsmittel benutzt habe.
3) die den benutzen Werken wörtlich und inhaltlich entnommenen Stellen als solche kenntlich gemacht habe.

Bremen, ____

II. Acknowledgements/Danksagung

I would like to thank my supervisors and the members of my thesis committee for their support and helpful advises: Tim Jennerjahn, Venugopalan Ittekkot and Kai Bischof as well as Matthias Zabel and Carlos Veiga de Cavalho.

Great thanks goes to my terrific working group: Gerti, Luci, Claudi, Ingo, David, Shilly, Anne and Daniela. Thank you for helping and inspiring me and for all the great advice you have provided within the last three years!

Glomar is gratefully acknowledged for the exciting courses they offer and for giving me the chance to attend the ATBC conference.

A very special thanks goes to the ones who helped me in the field in Indonesia and in the laboratory at ZMT: Carolin Herbon, Anne Buhmann, Daniel Wangprasseurt, Janina Korting, Ari Budi Santoso, Angela Maria Oviedo, Dana Pargmann, Alexandra Ostmann, Sonja Kleinertz as well as to the students from UNSOED Yuni, Andhi, Andri, Dendy, Zico, Edwin, Jefri, Rati, Dutha and Hendri and of course our great boat drivers Pak Hendro and Pak Mardi. Thanks so much – without you guys I would have never made it!

Not to forget our lab technicians at ZMT: Matthias Birkicht, Dorothee Dasbach, Christina Staschok and Silke Rick. Thanks for your help and support – especially to Matthias, who was always there when I needed him.

Thank you Petra Käpnick, Silke Eilemann and Gaby Böhme for organizing the flights (and for bringing me back ☺), Visa, travel expenses, etc., Uli Pint for the IT-support, Ago Merico for trying to improve a PhD candidates world as well as our new library fairy Christina Fromm. You are all doing a great job!

Thanks to Edy Yuwono, Hussein Sastranegara, Erwin Ardli and Claudia Schultz. I cannot say the field trips to Indonesia were always easy. Nevertheless you always tried to help and improved things!

As I am not a statistics expert I would like to thank Werner Wosniok for his inspiring ideas and his patience with all my statistic problems!

Thank you Martina, Gerti and Steffi for proof reading my thesis and for the advice you gave me.

… and last but not least …

The support for my PhD thesis is gratefully acknowledged above. But without my husband Alex and his great family Renate, Hans-Jürgen, Saskia and Kathi, my sister Frauke, her boyfriend Thorsten and our dad Werner and his wife Christine as well as my friends Marion, Artis, Régine, Mirko, Rocco, Peggy, Hendrik, Steph, Caro, Anne and Sarah I would never have made it. No words can describe how thankful I am to have such wonderful friends. Thanks for showing me everyday that friends are much more important than work! Or to say it in V. Nabokov´s (1899-1977) words: „Sobald man zum Thema von Dissertationen geworden ist, lebt man nicht mehr lange.“ I love you!

III. List of abbreviations/Abkürzungsverzeichnis

AA	*Avicennia alba*
AC	*Aegiceras corniculatum*
AI	*Acanthus ilicifolius*
AM	*Avicennia marina*
B	Penyu Bay
BG	*Bruguiera gymnorrhiza*
C	Central lagoon
CT	*Ceriops tagal*
DI	Degradation Index
DIN	Dissolved inorganic nitrogen
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DON	Dissolved organic nitrogen
DOM	Dissolved organic matter
DS	Dry season
DT	*Derris trifoliata*
Dw	Dry weight
E	Eastern lagoon
L	Light
M	Brown mangrove leaves
NUE	Nutrient use efficiency
OM	Organic matter
P	Rice plants

POC	Particulate organic carbon
POM	Particulate organic matter
R	Citanduy River
RA	*Rhizophora apiculata*
RE	Resorption efficiency
RI	Reactivity Index
RS	Rainy season
SAL	Segara Anakan Lagoon
SA	*Sonneratia alba*
SC	*Sonneratia caseolaris*
TDN	Total dissolved nitrogen
THAA	Total hydrolysable amino acids
THHA	Total hydrolysable hexosamines
TOU	Total oxygen uptake
TSM	Total suspended matter
W	Western lagoon
XG	*Xylocarpus granatum*

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V. Preface

The data used in this thesis were collected during 2004 – 2006 (SPICE [Science for the Protection of Indonesian Coastal Ecosystems] I) and 2007 - 2009 (SPICE II). This thesis entitled "Impact of mangroves and an agriculture-dominated hinterland on the carbon- and nutrient- biogeochemistry in the Segara Anakan Lagoon, Java, Indonesia" is a cumulative work, consisting of four papers: three papers are submitted and one manuscript is in preparation. Papers and manuscripts are presented as independent pieces of work. I provide information on the motivation and background to the work presented in this thesis and the material and methods used for both phases of the SPICE program, followed by an overarching framework on the implications for the Segara Anakan Lagoon. Furthermore, I present an outlook with upcoming questions resulting from this thesis and how to address these.

1. Summary

The current thesis was conducted within the German-Indonesian SPICE (Science for the protection of Indonesian Coastal Ecosystems) program. The research presented in this thesis is interdisciplinary in nature and combines both *in situ* and laboratory experiments and observations. The analytical tools include particulate carbon and nitrogen and their stable isotopes, dissolved inorganic nutrients (nitrate, nitrite, ammonium, phosphate and silicate), dissolved organic carbon (DOC) and nitrogen as well as amino acids. The research included investigations on a regional scale to fill the gaps in knowledge on carbon and nutrient cycling in the Segara Anakan Lagoon (SAL). Assuming this lagoon as a model system this thesis also provides information on sources and sinks, recycling processes, and tidal variations of carbon and nutrients for other mangrove ecosystems.

The SAL is mainly threatened by sedimentation, mangrove tree logging, overfishing and pollution. The lagoon receives input of nutrients mainly from the Citanduy River and exchanges water with the nutrient-poor Indian Ocean through an eastern and a western outlet. The lagoon size decreased by > 50% in the last 30 years due to high sedimentation rates. Most of the sediment is discharged as suspended matter through the Citanduy River in the western lagoon. A major part of this material derived from the agriculture-dominated hinterland as well as from the mangrove areas. The suspended material either accumulates in the lagoon and undergoes substantial degradation, or it is exported to the Indian Ocean.

The nutrient inventory has been investigated in the SAL over a period of five years. The nutrient distribution is mainly governed by the high inputs from the Citanduy River and therefore by the agriculture-dominated hinterland. Oceanic water only

influences the western lagoon during high spring tide, whereas the eastern outlet mainly receives water from the Indian Ocean through Penyu Bay. The Serayu River discharges into this adjacent bay and therefore indirectly influences the nutrient inventory of the eastern lagoon. The nutrient concentrations were significantly higher during the rainy season than during the dry season and displayed an east-west gradient. It has been shown that most of the nutrients are discharged through the Citanduy River and also that mangrove leaves leach high amounts of nutrients into the system. Despite high nutrient inputs the nutrient concentrations were low to moderate on a global scale and showed high variations between seasons and tidal cycles. Benthic recycling was not a major source of nitrogen, phosphate and silicate during the dry season when the river discharge is low. Nutrient sinks in the SAL were outwelling, assimilation by mangrove and shrub species, consumption by microbes, phytoplankton and phytobenthos.

Most likely due to mangrove tree logging a change in the vegetation structure has been observed in the last 25 years. Such a shift from true mangrove tree species to shrub species will alter the carbon and nutrient inventory in the lagoon. The two shrub species *Acanthus ilicifolius* and *Derris trifoliata* leached significantly more DOC and inorganic nutrients than the true mangrove tree species which might accelerate the nutrient turnover rates in the lagoon. This, in turn, can have a general effect on the whole food web and therefore the indigenous people who are highly dependent on an intact ecosystem.

Zusammenfassung

Diese Dissertation wurde im Rahmen des Deutsch-Indonesischen SPICE (Science for the Protection of Indonesian Coastal Ecosystems) Programms erstellt. Die in dieser Arbeit vorgestellte Forschung ist interdisziplinär. Die durchgeführten Analysen beinhalteten partikulären Kohlenstoff und Stickstoff und deren Isotopenzusammensetzung, gelöste anorganische Nährstoffe (Nitrat, Nitrit, Ammonium, Phosphat und Silikat), gelösten organischen Kohlenstoff (DOC) und Stickstoff sowie Aminosäuren. Die wissenschaftliche Arbeit beinhaltet Untersuchungen auf kleinskaligem Niveau, um Wissenslücken im Kohlenstoff- und Nährstoffkreislauf in der Segara Anakan Lagune (SAL) zu füllen. Diese Lagune kann als Modellsystem auch Informationen über Quellen und Senken, Recyclingprozesse und Tidenvariationen von Kohlenstoff und Nährstoffen für andere Mangrovenökosysteme liefern.

Die SAL ist durch Sedimentation, Mangrovenabholzung, Überfischung und Verschmutzung stark bedroht. Die Lagune erhält Nährstoffe und Sediment hauptsächlich durch den Fluss Citanduy im Westen und tauscht Wasser mit dem nährstoffarmen Indischen Ozean durch eine östliche und eine westliche Öffnung aus. Die Lagunenfläche verringerte sich in den letzten 30 Jahren aufgrund sehr hoher Sedimentationsraten um über 50, wobei das meiste Sediment vom Citanduy in die Lagune als suspendiertes Material eingebracht wird. Ein Großteil dieses Materials stammt sowohl aus dem agrarkulturdominierten Hinterland als auch aus dem Mangrovenbereich. Das suspendierte Material akkumuliert entweder in der Lagune und wird erheblich degradiert oder es wird in den Indischen Ozean exportiert.

Der Kohlenstoff- und Nährstoffbestand wurde über einen Zeitraum von fünf Jahren in der SAL untersucht. Die Nährstoffkonzentrationen sind hauptsächlich durch die hohen Einträge vom Citanduy und somit vom agrarkulturdominierten Hinterland geprägt. Meerwasser gelangt nur im westlichen Teil während der Springtide in die Lagune, wohingegen Wasser von der

angrenzenden Penyu-Bucht durch die östliche Öffnung eingetragen wird. Der Fluss Serayu fließt direkt in diese Bucht und beeinflusst somit indirekt die Nährstoffverteilung im östlichen Teil der Lagune. Während der Regenzeit waren die Nährstoffkonzentrationen signifikant höher als zur Trockenzeit und zeigten einen deutlichen Ost-West Gradienten. Es wurde nachgewiesen, dass sowohl ein Großteil der Nährstoffe durch den Citanduy eingetragen wird, als auch dass auch hohe Konzentrationen aus Mangrovenblättern ausgewaschen werden. Trotz des hohen Nährstoffeintrages war die Nährstoffkonzentration im globalen Vergleich niedrig bis moderat. Allerdings konnten große Unterschiede zwischen den Jahreszeiten und Tidenzyklen beobachtet werden. Während der Trockenzeit, wenn der Wasserzufluss durch Flüsse gering ist, war benthisches Recycling weder eine Quelle für gelösten Stickstoff, noch für Phosphat und Silikat. Nährstoffsenkend wirkten sich in der SAL der Nährstoffexport in den Indischen Ozean, die Assimilation von Mangrovenbäumen und Straucharten sowie die Aufnahme von Mikroben, Phytoplankton und Phytobenthos aus.

Voraussichtlich aufgrund der Mangrovenabholzung wurde eine Veränderung in der Vegetationszusammensetzung in den letzten 25 Jahren beobachtet. Eine solche Verschiebung von echten Mangrovenarten zugunsten von Straucharten wird den Kohlenstoff- und Nährstoffkreislauf zukünftig weiter beeinflussen. Die zwei Straucharten *Acanthus ilicifolius* und *Derris trifoliata* waschen signifikant höhere DOC und anorganische Nährstoffkonzentrationen aus als echte Mangrovenarten, was voraussichtlich zu einem schnelleren Nährstoffumsatz führt. Dies wiederum kann einen Effekt auf das gesamte Nahrungsnetz und somit indirekt auch für die einheimische Bevölkerung haben, die auf ein intaktes Ökosystem angewiesen sind.

2. Introduction

2.1 Motivation: The global importance of tropical mangrove-fringed lagoons

Mangroves are a highly valuable ecological and economic resource, an important nursery ground and breeding site for various animals, a renewable source of wood, an accumulation site for sediment, contaminants, carbon and nutrients. They offer protection against coastal erosion, strong storms and tsunami events, and stabilise dynamic shorelines (Ayukai et al. 1998, Alongi 2002, 2008, Alongi & Carvalho 2008, Bouillon et al. 2008). They decline at a rate of ~2% per year due to urban development, aquaculture, mining, and overexploitation for timber, fish, crustaceans and shellfish (Saenger et al. 1983, Valiela et al. 2001, Alongi et al. 2005). Mangroves are highly productive and present ~75% of the world's tropical and subtropical coastline with an estimated area of 1.7 x 10^5 km^2 (Odum & Heald 1975, Duarte & Cebrián 1996, Valiela et al. 2001, Marchand et al. 2006). This high productivity is among others due to high solar radiation and temperatures, a year-long growing season and generally abundant nutrients in the soil (Day et al. 1987). Mangrove plant litter comprises about 30 to 60% of the total tree production (Duarte & Cebrián 1996). Typical global average litterfall rates are on the order of ~38 mol C m^{-2} yr^{-1} (Jennerjahn & Ittekkot 2002). About half of the produced mangrove plant litter is exported to adjacent coastal waters (Robertson et al. 1992, Duarte & Cebrián 1996, Dittmar & Lara 2001a, Jennerjahn & Ittekkot 2002). This detrital material serves as the base for food webs in estuarine and coastal environments (Odum & Heald 1975, Rodelli et al. 1984, Alongi et al. 1989).

The investigation of biogeochemical cycles in aquatic systems is an ideal tool to understand the response of tropical coastal ecosystems to environmental changes, both natural and anthropogenic. Coastal ecosystems like mangroves link terrestrial and marine biogeochemical cycles. Its vegetation is important in contributing organic matter (OM) to its associate biota as well as to the adjacent ecosystems via tidal exchanges (Odum & Heald 1975, Basak et al. 1998, Jennerjahn & Ittekkot 2002, Dittmar et al. 2006).

So far, studies on mangrove ecology are scarce. It is important, however, to better understand the ecological interactions in mangroves to be able to provide reliable global carbon and nutrient budgets. In this thesis, the sources and sinks of dissolved inorganic nutrients (nitrate, nitrite, ammonium, phosphate, and silicate) and of OM including their possible input through leaf leaching, riverine input, and benthic recycling in the Segara Anakan Lagoon (SAL) are defined. By using analytical tools like particulate and dissolved carbon and nitrogen and their stable isotopes, dissolved inorganic nutrients and amino acids some gaps in knowledge on carbon and nutrient cycling in the SAL can be filled or at least reduced. Taken the SAL as a model system, this can help creating an image on recycling processes in Indonesian mangroves as well as on the contributions of dissolved organic carbon (DOC) and nutrients to coastal ecosystems. The work requires to follow the suspended and dissolved matter from their source to their sinks, e.g. from the mangrove primary producers through the food web and finally to either the local sediment or, due to outwelling, to the sediments of the adjacent coastal ecosystem.

The lack of long-term data is the major obstacle in predicting mangrove responses to human impacts. Also, it is the difficult to distinguish natural from anthropogenic changes. Furthermore, whole-ecosystem mass balances for carbon, nitrogen and phosphorus as well as information on secondary production, on species diversity of flora and fauna as well as on effects of excess nutrients on mangrove growth and survival are scarce (Alongi 2002). As the SAL suffers from various anthropogenic impacts like industry, households, and overexploitation of natural resources, it is a prerequisite to understand and evaluate different needs of and on this ecosystem as well as to find solutions which satisfy different stakeholders and also to keep a balanced ecosystem.

The current thesis provides a description of nutrient and carbon dynamics in the SAL, which could help to establish better management strategies (**paper 2** and **3**). It will be further explained why the findings presented in this thesis are relevant not only for this specific study site but also for other mangrove ecosystems. In p**aper 1** and **4** a leaching study using eight mangrove and shrub species will be presented. To this extent such a study has not been conducted before. These results are of great benefit for other studies on mangrove ecosystems, especially for those which calculate global budgets. The effects of the temporarily varying river loads on the biogeochemistry of the lagoon with regard to seasonality, tidal variations, and benthic recycling processes are presented in **paper 2**. This will contribute significantly to the scientific understanding on mangroves since so far studies on seasonality over years and on tidal variations are rare. Therefore, the findings presented in this thesis will not only help to understand ecological interactions on a small scale but are also globally relevant.

2.2 Carbon and nutrient cycling

Most of the total carbon present on Earth is stored in soils and does not undergo active biogeochemicaly mediated exchange processes (Hedges 1992). The major part of OC is generated by photosynthetic fixation of atmospheric CO_2 by terrestrial plants and marine phytoplankton (Seiter et al. 2004). This OC goes through the different trophic levels of the biosphere and ends with the metabolic or chemical oxidation of decayed biomass to CO_2 (Zabel & Hensen 2006). A detailed description on the global carbon cycle with regard to pre and post-industrial times can be found in e.g. Siegenthaler and Sarmiento (1993).

In the Indo-West Pacific most mangroves occur in estuaries with mostly very turbid waters. There and in near mangrove wetlands, the carbon and energy fixed by mangrove vegetation is the most important nutrition for organisms (Saenger et al. 1983, Robertson et al. 1992). The mangrove leaves can either be decomposed by microbes, consumed by the local fauna or exported to adjacent ecosystems (e.g. Odum & Heald 1975, Robertson et al. 1992, Jennerjahn & Ittekkot 2002). An example of the carbon stock and fluxes in a mangrove forest (Missionary Bay, Australia) is presented in **Fig. 1**.

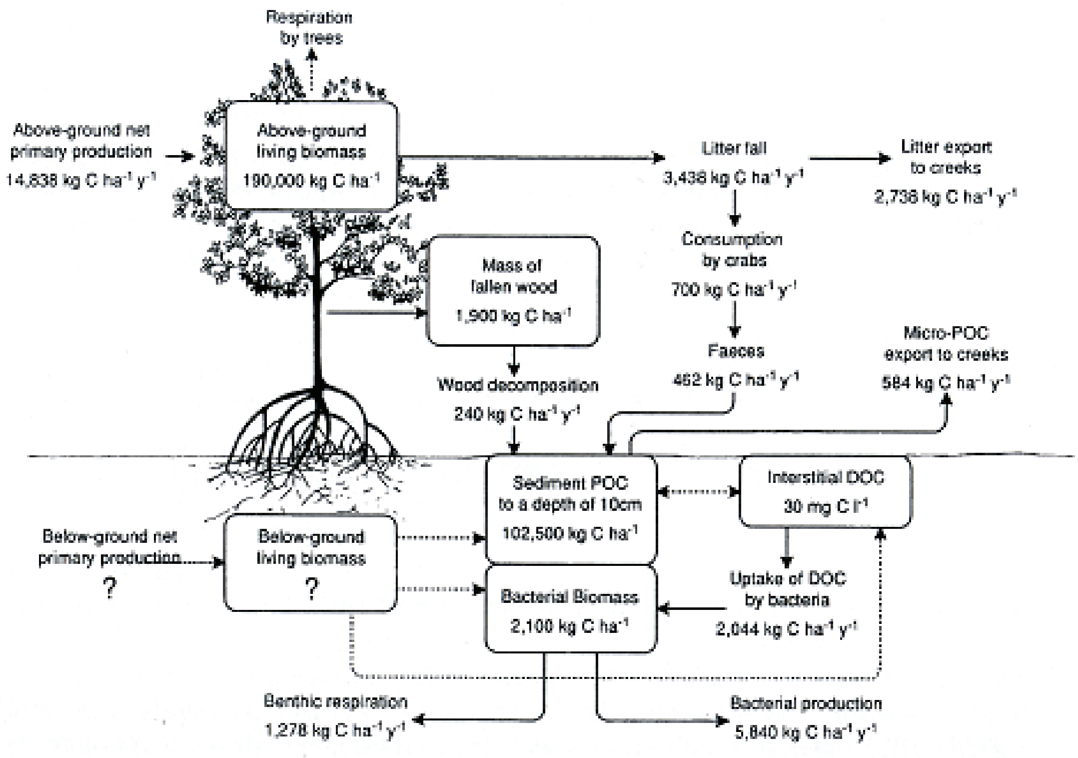

Fig. 1: Major carbon stocks [kg C ha^{-1}] and carbon fluxes [kg C ha^{-1} y^{-1}] in a mangrove forest in Missionary Bay, Australia (Robertson et al. 1992).

Mangroves and other coastal ecosystems are threatened by eutrophication. Due to anthropogenic inputs nutrient concentrations increased steadily in recent decades (Moffat 1998, Seitzinger et al. 2005, Gupta et al. 2006, Seitzinger et al. 2010). They can originate from riverine and agricultural sources, industrial and urban sewage and atmospheric deposition as well as from natural sources like fixation of atmospheric nitrogen by cyanobacteria and release by microbial decomposition or organic material (Howarth et al. 1996, Hogarth 2007). Nitrogen can be present in different organic and inorganic forms (**Fig. 2**). Various biogeochemical processes are included in nutrient cycling like denitrification, N-fixation, pelagic and benthic productivity, organic matter sedimentation and burial, pelagic and benthic respiration and sediment-water fluxes (e.g. Eyre 2000a, Pederson et al. 2004). Assimilated nutrients by plants are temporarily immobilized and therefore unavailable for other biogeochemical processes (Pederson et al. 2004). These nutrients are lost through export of detritus or they can be remineralized through grazing and decomposition (Duarte & Cebrián 1996).

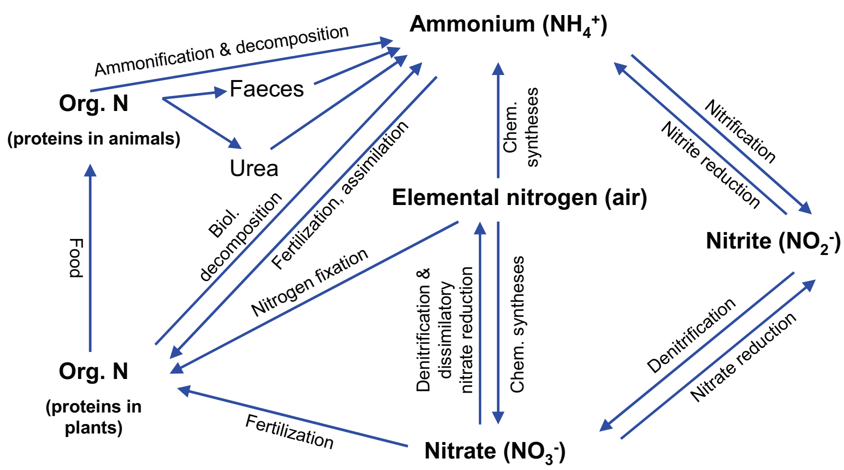

Fig. 2: Nutrient cycling between atmospheric, organic and inorganic nitrogen.

Dissolved organic matter (DOM) and nutrients can be exchanged between intertidal areas and the water column either by diffusive fluxes across the sediment-water interface during inundation or by pore water seepage into the water column during low tide (Ovalle et al. 1990, Bava & Seralathan 1999, Lara & Dittmar 1999, Bouillon et al. 2007a, Bouillon et al. 2007b, Chen et al. 2007). Sediments are assumed to play a major role in the transformation of biological active elements, especially for processing nitrogen during OM degradation in estuaries (Lock & Hynes 1976, Sloth et al. 1995).

2.3 The Segara Anakan Lagoon

The SAL (108°46´E – 109°03´E, 7°35´S – 7°48´S; **Fig. 3**) is the largest remaining mangrove stand on the south coast of Java with an area of >9000 ha in 2006 (Ardli & Wolff 2009). The hydrology of the lagoon is governed by seasonally varying river runoff of the Citanduy River in the west and tidal exchange with the Indian Ocean through two channels in the eastern and western part of the lagoon (White et al. 1989, Yuwono et al. 2007a). The freshwater input from the Citanduy River and the exchange with oceanic waters are responsible for varying salinities and the suspended sediment load. The Citanduy is the fifth largest river of Java in terms of discharge, which is estimated to 227 m^3 s^{-1} (Yuwono et al. 2007a, Holtermann et al. 2009). The Donan catchment area in the eastern area has a freshwater input two orders of magnitude less than the Citanduy (Holtermann et al. 2009). The central lagoon is affected by both, tidal water movement and by the discharge of the rivers Citanduy, Cibereum and Cikonde (Purba 1991, Yuwono et al. 2007a). The climate is divided into a rainy season (November till March, annual precipitation: 3000-3500 mm) and a dry season (April till October) (White et al. 1989, Whitten et al. 2000).

The SAL is threatened by various factors like overfishing, logging of mangrove wood or pollution by pesticides and oil as well as by high sedimentation rates. Already in the 19th century, the lagoon became narrower and shallower. Especially the Citanduy River transported high sediment loads due to unsustainable land-use practices in the hinterland (Yuwono et al. 2007b). Additionally to the sediment input, the lagoon is endangered by the conversion of mangrove area into rice fields and aquaculture which was estimated to be ~52% since 1978 (Ardli & Wolff 2009).

In the SAL 21, mangrove tree species and five understorey genera occur (White et al. 1989, Hinrichs et al. 2008). Within the last 25 years, the shrub species *Acanthus ilicifolius* and *Derris trifoliata* spread into the SAL and are nowadays even more abundant than true mangrove tree species. These shrubs generally occur in mangrove ecosystems with natural and human disturbances since gaps, e.g. due to logging, are rapidly occupied by them (Hogarth 2007). Further information on the study area is given in the four papers published from this thesis, as well as in former studies (Yuwono et al. 2007a, Hinrichs et al. 2008, Ardli & Wolff 2009, Holtermann et al. 2009, Jennerjahn et al. 2009a).

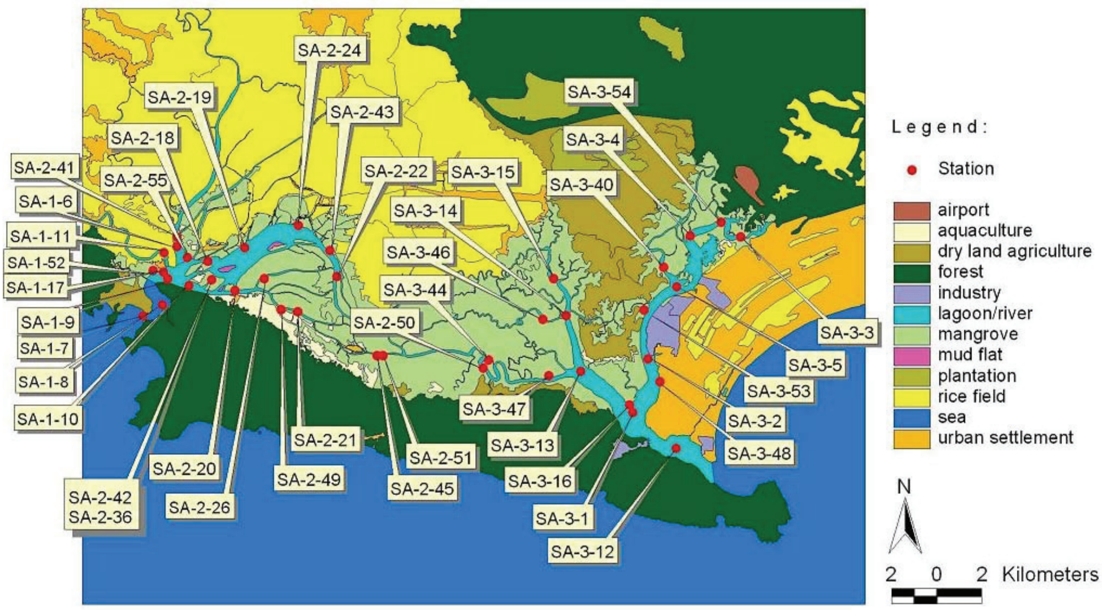

Fig. 3: Map of Segara Anakan showing different land types, the Indian Ocean, and the different sampling stations.

2.4 Scientific objectives

This thesis was conducted within the German- Indonesian SPICE (Science for the Protection of Indonesian Coastal Marine Ecosystems) II-program. The main objective of this part of the program was to contribute to the development of strategies for the sustainable use of living resources in the SAL. Since a detailed knowledge on the ecosystem structure as well as the interactions of the social and economic connection was missing in this lagoon, so far no sustainable working management plan was established. Within the framework of the SPICE-II-program, I investigated the seasonal and spatial variations in biogeochemical processes in the SAL. An extensive examination of the biogeochemical cycles regarding anthropogenic influences, seasonal variations, regional differences (e.g. river discharges) and estimation of ecological changes in the SAL is the prerequisite for a sustainable use of this area and for improving the management of the lagoon.

Therefore, the following research questions were addressed:

1) What are the sources and sinks of nutrients and organic carbon and what are their spatial and temporal variations?
2) Which patterns influence the sedimentation in the SAL and what is the origin of the sediment?
3) What might be the impact of a change in the vegetation structure on the carbon and nutrient inventory in the lagoon?

A list of the four publications, the research questions and the topics addressed as well as the methods used to answer these questions is presented in **Tab. 1**.

Tab. 1: Topics addressed and the methods used for each of the four publications.

Paper no.	Research Question	Paper topic	Topics addressed	Method
1	1,3	Leaf leaching of dissolved organic carbon from eight plant species in the mangrove-fringed Segara Anakan Lagoon, Java, Indonesia	• DOC input from leaves into the SAL • Possible impacts of habitat destruction for the SAL • Impact factors on leaching • Interspecific differences between mangrove tree and shrub species	• Leaf leaching experiment • Impact factor: salinity
2	1	Nutrient dynamics in the Segara Anakan Lagoon, Java, Indonesia	• Spatial and temporal variation of the nutrient inventory of the SAL • Sources and sinks of nutrients • Benthic recycling	• Nutrient sampling over a five year period • Incubation experiment • 24 h nutrient sampling during spring and neap tides
3	1; 2	Fate of organic matter derived from mangroves and from an agriculture-dominated hinterland in the Segara Anakan Lagoon, Java, Indonesia	• Determination of the sources of the sediment causing a decrease in lagoon size • Transformation processes of organic matter • Seasonal variation in the biogeochemical composition of TSM and its sources	• Sources: determined by using the C/N ratio and the stable isotope approach • Diagenetic status: determined by using the reactivity index of amino acids
4	1, 3	Leaching of dissolved inorganic nutrients from eight mangrove and shrub species in the Segara Anakan Lagoon, Java, Indonesia	• Nutrient input from leaves into the SAL • Possible impacts of habitat destruction for the SAL • Impact factors on leaching • Interspecific differences between mangrove tree and shrub species	• Leaf leaching experiment • Impact factor: salinity

3. Material and methods

3.1 Water and sediment sampling

Samples were taken during SPICE I (2004 to 2006) and SPICE II (2007 to 2009) during the dry and rainy seasons. The data used from SPICE I were collected during May 2004, January 2005, August 2005, and August 2006. During SPICE II samples were taken in September 2007, February and September 2008 as well as February and September 2009 (**Fig. 4**).

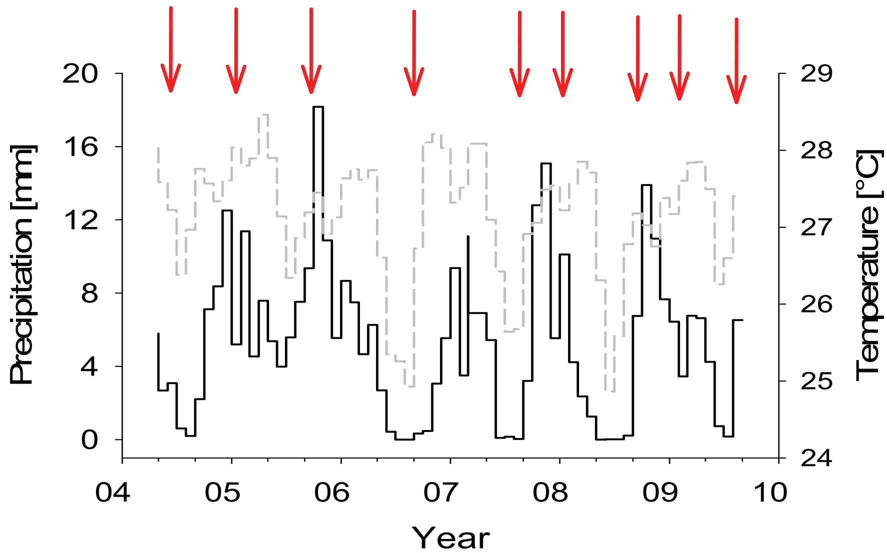

Fig. 4: The mean precipitation [mm] and temperature [°C] in the city of Cilacap during both SPICE phases. Red arrows denote sampling campaigns (source: http://climate.usurf.usu.edu/).

Surface water samples were taken at 23 stations in the SAL aboard a fisherman's boat. The abiotic parameters temperature [°C], conductivity [mS cm^{-1}], oxygen content [mg l^{-1}] and pH were measured *in situ*. The WTW pH and oxygen probe was calibrated daily.

50 ml of surface water for inorganic nutrients (ammonium, nitrate, nitrite, phosphate and silicate) analysis were filtered through syringe filters (pore size 0.45 µm) into PE-

wide neck bottles, preserved with a 4% mercury chloride solution and stored dark and cool until analysis. 10 ml of surface water were filtered also through syringe filters into pre-annealed glass ampullae (~4 h at 500°C) and treated with 1 M hydrochloric acid for DOC and total dissolved nitrogen (TDN) analysis. The ampullae were weld up and stored dark and cool until measurement.

A PE-container was filled with surface water and stored dark and cool until return to the laboratory where the water was filtered on pre-weighed and combusted Whatman GF/F filters (particle retention: 0.7 µm) for particulate organic carbon (C_{org}), total particulate nitrogen (N), isotopic composition ($\delta^{13}C_{org}$ and $\delta^{15}N$), amino acid and chlorophyll a analyses.

Sediment samples were taken with an Ekman grab. About 15 g of sediment surface were put into pre-annealed glass vials (~4 h at 500°C) and dried at 40°C for total and organic carbon, total nitrogen and amino acid analysis. About 50 g of sediment surface were taken for grain size analysis and stored wet and air-free in zip-loc bags.

3.2 Analysis

The following devices and methods were used during the current study as well as during SPICE I. An overview of the sampling, the treatments and devices used is presented in **Fig. 5** and an overview of the devices used during the two SPICE phases in given in **Tab. 2**.

<u>3.2.1 Abiotic:</u> Conductivity [mS cm^{-1}], dissolved oxygen (DO) [mg l^{-1}], pH and temperature [°C] were measured with a WTW MultiLine 340i multiparameter instrument (**paper 2** and **3**). The same instrument type was used during 2004 to 2006. The salinity was calculated with conductivity and temperature, the oxygen saturation [%] with dissolved oxygen content, pressure and temperature.

Tab. 2: The methods used for measuring different parameters during SPICE I and II.

Parameter	**Method**	**SPICE I**			**SPICE II**		
		2004 - 2006	Sep. 07	Feb. 08	Sep. 08	Feb. 09	Sep. 09
Abiotic	WTW MultiLine 340i	X	X	X	X	X	X
DOC	Apollo 9000	X	X	X	X	X	-
	Shimadzu	-	-	-	-	-	X
Nutrients	Manually (after Grasshoff and Koroleff 1996)	-	X	-	-	-	-
	SKALAR-SANplus	X		X	X	X	X
C_{org} and N	Carlo-Erba NA 2100	X	X	X	X	X	X
Isotopes	Carlo Erba Flash EA 1112	X	X	X	X	X	X
Amino acids	Biochrome B30	-	-	-	-	X	X
Grain size	Horiba LA300 (ZMT)	X	-	X	-	-	-
	Beckmann-Coulter (MARUM)	-	X	-	-	X	-
Chlorophyll	Fluorometer	-	X	X	X	X	X
	Unknown (measured in Indonesia)	X	-	-	-	-	-

3.2.2 DOC: The DOC and TDN samples collected during September 2007, February and September 2008 and February 2009 were combusted in a Teledyne Tekmar Apollo 9000 Combustion analyzer at 680°C (**paper 1** and **2**). The samples taken during September 2009 were combusted in a Shimadzu TOC-V CPH at 720°C. No significant differences were found between both devices (Birkicht pers. comm.).

3.2.3 Nutrients: Inorganic nutrient samples were measured manually after Grasshoff and Koroleff (1996) during the first expedition in September 2007 as well as during the 24 h samplings in December and January 2008 (tidal variations, **paper 2**). The samples collected during the following four expeditions were measured with an elemental autoanalyzer SKALAR-SANplus system (**paper 2** and **4**) and detected spectrophotometrically as a coloured complex. This device was also used during 2004 and 2006 (these data are included in **paper 2**). Ammonium could not be detected since the concentrations were below the detection limit. Therefore dissolved inorganic nitrogen (DIN) consists in the following of nitrate and nitrite (determination limits: nitrate: 0.04 µM, nitrite: 0.05 µM, ammonium: 0.06 µM, phosphate: 0.06 µM and silicate: 0.19 µM; coefficient of determination: <3.4%). However, silicate measurements highly depend on the pH of the samples (Birkicht pers. comm.). Even though the pH of all samples was measured a pH adjustment of all chemicals used for this analysis could not be performed due to the high number of samples. Therefore it is possible that some silicate concentrations were overestimated (**paper 2** and **4**).

3.2.4 C_{org}, N, $\delta^{13}C_{org}$ and $\delta^{15}N$: Particulate carbon (total and organic) and nitrogen were analyzed using a Carlo-Erba NA 2100 Elemental Analyzer. For analyzing the isotopic composition of C_{org} and N (**paper 3**) a Thermo Finnigan Delta^{plus} mass spectrometer combined with a Carlo Erba Flash EA 1112 elemental analyzer via ConFlo III interface was used (analytical errors: C_{org} <0.1%, for N <0.01, for $\delta^{13}C$ and for $\delta^{15}N$ <0.2‰). This device was also used during 2004 and 2006 (these data are included in **paper 3**).

3.2.5 Amino acids: Both filter and sediment samples from February and September 2009 were analyzed for total hydrolysable amino acids (THAA) and total hydrolysable hexosamines (THHA) (**paper 3**). THAA and THHA were quantified by a low pressure ion exchange chromatography *Biochrome B30*. The samples were hydrolyzed with 6 N HCl for 22 h and the aliquot was evaporated, filled with distilled water and evaporated again (analytical errors for the amino acids and hexosamines <6%). However, THAA are included in proteins but are also bound in some other chemical or physical matrices and can be released from there during acid hydrolysis (**paper 3**). For this reason, THAA measurements may not accurately reflect the protein that is available for biological remineralization (Pantoja & Lee 2003). The use of THAA as an indicator for material freshness is not always straight forward as diagenesis also entails the synthesis of amino acids through the production of microbial biomass (Keil and Fogel, 2001; Macko et al., 1994).

3.2.6 Grain size: For grain size analysis the sediment samples were heated in distilled water at >90°C for two minutes in $NaPO_4$ to avoid particle clogging. The sediment grains were divided into sand (2000 – 63 µm), silt (63 – 2 µm) and clay (<2 µm). Sediment grain sizes were either measured with a laser diffraction particle analyzer (Beckmann-Coulter LS3200) at the MARUM, measuring particles between 0.38 – 2000 µm, or with a Horiba LA300 laser scattering particle size distribution analyzer at ZMT, with a particle range of 0.1 – 600 µm. Comparing both devices did not reveal statistically significant differences (Birkicht pers. comm.). The grain size data are not presented in the four papers of this thesis but statements on the grain size distribution of the three lagoon areas are made in **paper 3**.

<u>3.2.7 Chlorophyll a:</u> The GF/F filters were cut and the suspended matter on the filter was dissolved in 9 ml acetone (90%), stored cold and dark for 24 hours and centrifuged. The particle-free solution was measured with a Turner 10-AU fluorometer (**paper 2**).

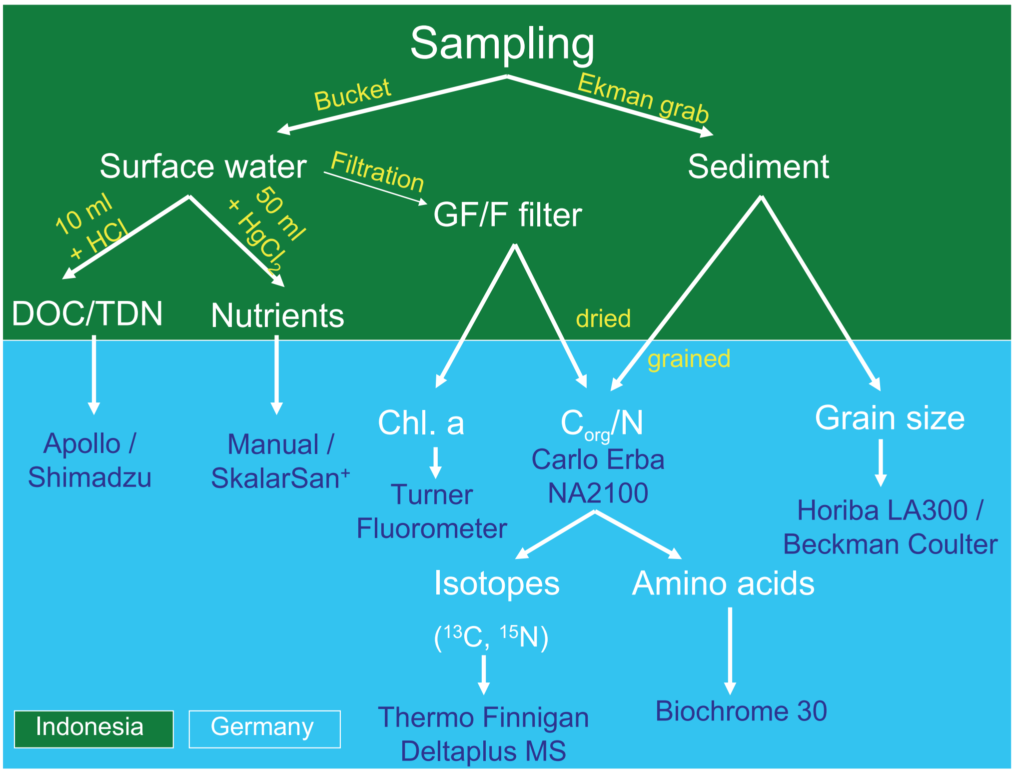

Fig. 5: Overview of the sample types, treatments and analysis (green: Indonesia, blue: Germany).

3.3 Experiments

<u>3.3.1 Leaf leaching experiment:</u> A leaf leaching experiment (**Fig. 6**) was conducted with leaves from the six mangrove and two shrub species. Each leaf was weighed before the start of the experiment. One leaf at a time was submerged in glasses containing 400 ml of artificial sea water at four salinities: 0, 10, 20 and 30 g l^{-1}. Leaves were removed from the glasses at eight times (10 sec, 2 h, 6 h, 1 d, 3 d, 7 d, 15 d, and 30 d). For each experimental approach three replicates were prepared. After removing the leaves they were dried at 40 °C and weighed again to calculate the

weight loss. A detailed description of the experimental setup can be found in **paper 1** and **4**.

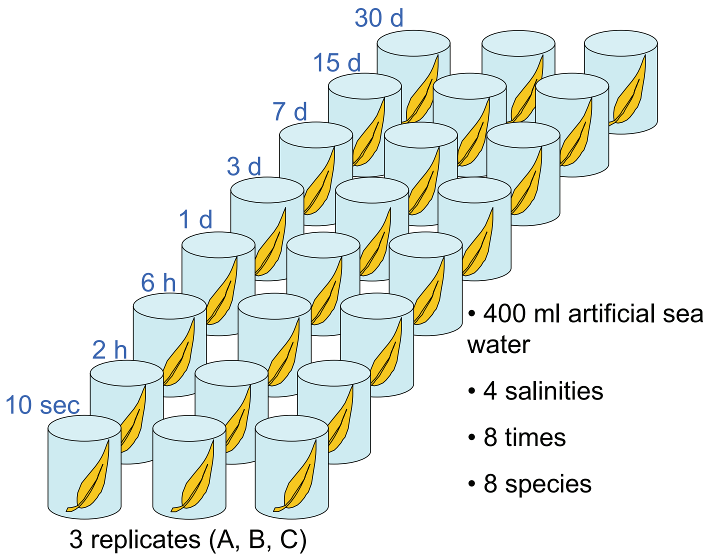

Fig. 6: The experimental set up of the leaf leaching experiment presented in **paper 1** and **4**.

The data in **paper 1** and **4** revealed a great variability between the three replicates. Therefore, a higher number of replicates would be more sufficient to explain differences between species over time. The leaves in these experiments were not washed before the experiment so that microbes were brought into the system.

For the nutrient leaching experiment (**paper 4**) a blank over 30 d would have been necessary to exclude an influence of the glass on the nutrient concentrations. It is known that glass can release significant silicate concentrations. Therefore, glasses were filled with water at four salinities (0, 10, 20 and 30 g l^{-1}) at the ZMT and silicate concentrations were measured after 15 and 30 d. The experiment did not show a high impact of glass on the silicate concentrations in the water. Nevertheless, since the glasses used there were not the same than those used in the leaching experiment conducted in Indonesia an impact of glass can not be excluded totally.

<u>3.3.2 Core incubation experiment:</u> Three plexiglass cores were taken for an incubation experiment to determine benthic recycling rates of inorganic nutrients (**Fig. 7**). Two cores contained half sediment and half lagoon water of which one core was wrapped in dark tape. A third core contained lagoon water only. The three cores were sealed with lids on the upper and lower end. The upper lid was prepared with two plastic tubes of which one was attached to a syringe for sampling and the other one with a plastic bag which contained lagoon water. Samples were taken over a 24 h period. Due to problems with the electrical pumps the water in the cores was mixed manually by a gentle drawing up the syringe and pressing the water into the core again before sampling. During this procedure the attached water bag was sealed with a one-way-plug and opened again for sampling to replace the taken water volume. At each sampling time 20 ml of water were taken from the core with the syringe to measure the oxygen content with an oxygen electrode as well as inorganic nutrients and DOC concentrations. A detailed description of the experimental setup is presented in **paper 2**.

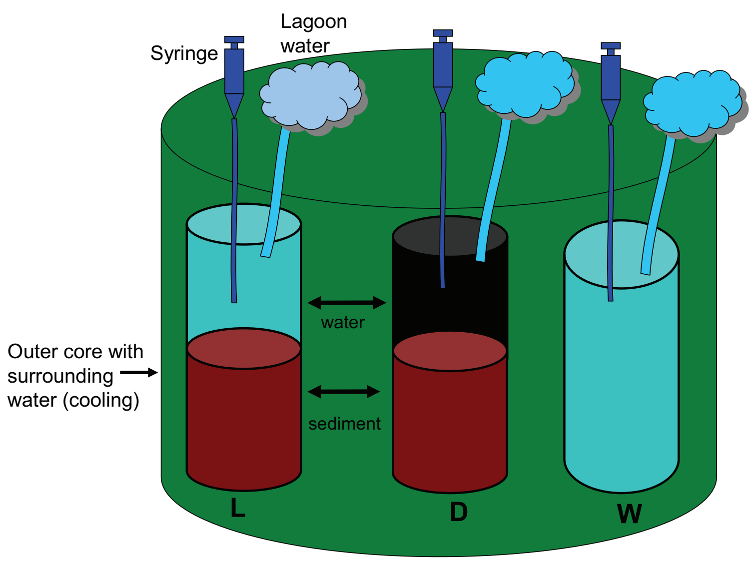

Fig. 7: The experimental setup of the incubation experiment with benthic chambers presented in **paper 2** (L= light, D= dark, W= lagoon water).

3.3.2.1 Phytobenthos, phytoplankton and bacteria: The fluxes presented in **paper 2** were much lower compared to other studies and did not reveal any differences between the three treatments. It has been shown in a study on dinoflagellates that the uptake of nitrate and ammonium is species dependent (Paasche et al. 1984). Also heterotrophic bacteria can take up substantial amounts of ammonium but a utilization of nitrate is rather unlikely (Probyn et al. 1996 and references therein). However, no further attempt was made in the current thesis to examine the phytoplankton, phytobenthos and the bacterial biomass and therefore their impact on the flux rates. Besides the uptake by phytoplankton, phytobenthos and bacteriobenthos also the benthic mineralization of dead cells which lead to a nutrient release into the interstitial or overlying water column can affect the calculation of the flux rates (Kelderman et al. 1988, Alongi et al. 1993, Ovalle et al. 1999). Therefore the fluxes presented in **paper 2** are an interaction of efflux from porewater as well as uptake and release by organisms.

3.3.2.2 Experimental conditions: Experimental conditions can lead to differences in benthic flux rates like light intensity (MacIntyre & Cullen 1995, Cahoon 1999) or the stirring rates (Devol 1987, Sweerts et al. 1989). In most of the studies used for a global comparison in **paper 2** the light intensity was not mentioned. This might be a major reason for differences in flux rates from the literature rather than natural conditions. In the benthic recycling experiment the water was stirred periodically and not continuously due to problems with the pumps. However, Campbell and Rigler (1986) found that mixing and a constant flow is required for realistic sediment oxygen consumption measurements. Nevertheless, it has also been shown that enclosure and artificial stirring did not seriously alter benthic exchange rates (Devol 1987, Corroder

& Morell 1989). It remains unclear whether the periodically stirring affected the flux rates in our study.

Different authors used different experimental approaches like intact or disturbed sediment cores, benthic chambers or bell jars (Kelderman et al. 1988, Alongi 1991, Alongi et al. 1993, Davis III et al. 2001, Gardner & McCarthy 2009). In addition, the duration of incubation varied between the studies from a few hours up to several days. Calculations and units also differ between the investigations and might therefore not be comparable. So far there is no conventional method for measuring primary production of flux chambers (Nowicki & Nixon 1985, Underwood & Kromkamp 1999). This can result in difficulties when comparing the data in the current thesis with those from the literature.

4. Discussion

4.1 Sources and sinks of nutrients and organic matter and global incorporation of the SAL

In **paper 2** nitrogen and silicate concentrations in the SAL has been presented, displaying a strong west-east gradient. It has been assumed earlier that the Citanduy River represents a major source of nutrients into the lagoon (Yuwono et al. 2007a, Jennerjahn et al. 2009b). The high nutrient concentration in this river might also be responsible for the slightly higher fluxes at the sediment-water interface at the two stations in the western and central area. However, as fluxes were extremely low throughout the SAL benthic recycling was not an important nutrient source during the dry season 2009.

A high possible input of nutrients from leaf leaching into the lagoon has been shown in **paper 4.** The following calculation is highly speculative but it emphasizes a possible input of carbon and nutrients by leaf leaching in the SAL. Litterfall rates were determined by the Master student Angela Maria Oviedo during the rainy season 2008. The data might not represent the true litterfall as some littertraps were stolen so that the data bear statistical uncertainties. Nevertheless, litterfall rates were in the same range as found in other mangrove areas (Twilley et al. 1986, Saenger & Snedaker 1993, Bunt 1995, Sharma et al. 2010). The litterfall rates, the maximum DOC and the maximum nutrient leaching concentrations from **paper 1** and **4** are shown in **Tab. 3**. Taken the average flux values of the eight species investigated in this thesis a PO_4^{3-} flux of 0.32 µM m^{-2} d^{-1}, a DIN flux of 1.74 µM m^{-2} d^{-1} and a $Si(OH)_4^-$ flux of 39.65 µM m^{-2} d^{-1} can be calculated. Assuming a mangrove area of 9,000 ha (data from 2006; Ardli & Wolff 2009) this results in an average PO_4^{3-} flux of

Tab. 3: The litterfall rates and maximum DOC and nutrient concentrations leached from different species and the resulting fluxes. Litterfall estimations for *Avicennia spp*. were used for the calculations of *Avicennia marina* fluxes and those estimated for *Sonneratia spp.* for *Sonneratia caseolaris* fluxes (AC= *Aegiceras corniculatum*, AI= *Acanthus ilicifolius,* AM= *Avicennia marina*, BG= *Bruguiera gymnorrhiza*, CT= *Ceriops tagal*, DT= *Derris trifoliata*, RA= *Rhizophora apiculata*, SC= *Sonneratia caseolaris*).

species	Litterfall [g (dw) m^{-2} d^{-1}]	DOC [mM g^{-1} dw]	PO_4^{3-} [µM g^{-1} dw]	DIN [µM g^{-1} dw]	SI(OH)4 [µM g^{-1} dw]	DOC flux [mM m^{-2} d^{-1}]	PO_4^{3-} flux [µM m^{-2} d^{-1}]	DIN flux [µM m^{-2} d^{-1}]	Si flux [µM m^{-2} d^{-1}]
AC	0.12 (± 0.21)	34.74	4.78	18.39	476.16	4.20	0.58	2.23	57.62
AI	0.05 (± 0.09)	115.13	8.72	64.69	1278	6.10	0.46	3.43	67.73
AM	0.02 (± 0.01)	53.60	7.55	22.55	359.53	0.80	0.11	0.34	5.39
BG	0.03 (± 0.00)	4.46	4.24	3.55	29.22	0.12	0.12	0.10	0.82
CT	0.04 (± 0.09)	38.84	7.25	47.86	895.64	1.71	0.32	2.11	39.41
DT	0.04 (± 0.06)	31.24	-	77.17	1126.8	1.16	-	2.86	41.69
RA	0.17 (± 0.15)	14.02	2.81	12.21	452.08	2.36	0.47	2.05	75.95
SC	0.03 (± 0.05)	21.94	7.17	32.61	1142.34	0.55	0.18	0.82	28.56

$28*10^6$ µM d^{-1}, a DIN flux of $157*10^6$ µM d^{-1} and a $Si(OH)_4^-$ flux of $4*10^9$ µM d^{-1} for the entire lagoon. This shows a very high possible input of nutrients into the SAL. However, compared to the flux calculations presented in **paper 2**, these phosphate and nitrogen fluxes are much lower than those reported for the Citanduy River during the rainy season (PO_4^{3-}: ~0.3%, DIN: ~0.01%). Silicate fluxes from leaves, though, were higher than those calculated for the river ($Si(OH)_4^-$: 357%). It has to be considered that these are maximum estimations as the mangrove area size probably decreased since 2006. Furthermore, the data presented here for the flux calculations base only on data collected during the rainy season. The leaching of nutrients from leaves is, therefore, not the major source during the rainy season when the river discharges high nutrient concentrations. It can, however, be an important source in the eastern lagoon, where the impact of the Citanduy River is limited. Here, the input from leaching can probably balance the nutrient loss by export that was determined during the rainy season. In the dry season when the river discharge is low leaf leaching might also be an important nutrient source in the western area. However, no flux data for the dry season are available for a comparison.

The high nutrient concentrations in leaves suggest that mangrove trees are not only a source but also a sink for nutrients. It is known that freshwater and marine angiosperms require a C:N:P ratio of 435:20:1 (Duarte 1992), which indicates that more nitrogen is needed in relation to phosphorus compared to the Redfield ratio for phytoplankton. However, as has been shown in **paper 2,** the nutrient inventory of the SAL revealed a N:P ratio of 33 during the rainy season and 13 during the dry season. Therefore, the mangroves are rather phosphate limited during the rainy season and nitrogen limited during the dry season. However, a more appropriate measure to determine nutrient limitation would be the N:P ratio of leaves and not of the surrounding waters (Tessier & Raynal 2003). Microbes and fungi were also assumed to consume high amounts of nutrients and consequently to function as a nutrient sink (**papers 2** and **4**). This assumption was based on the results in other studies (Kohlmeyer 1969, Twilley et al. 1986, He et al. 1988, Robertson 1988, Alongi et al. 1989, Kaye & Hart 1997). Thus, nutrient uptake by the different organisms can be responsible for the rather low to moderate nutrient concentration in the lagoon (**paper 2**, Jennerjahn et al. 2009, see also 5.2.1). Even more important is probably the short residence time of the water in the SAL (Holtermann et al. 2009). It is likely that outwelling of nutrients is the major reason for the rather low nutrient concentrations in the lagoon in relation to the high nutrient input from the agriculture in the hinterland as well as from leaf leaching.

It has been stated that the SAL was in an oligotrophic to eutrophic state between 2004 and 2006 applying the criteria of Smith et al. (1999) (Jennerjahn et al. 2009a). Based on the nitrate and phosphate concentrations during 2007 and 2009 the lagoon was purely oligotrophic (**Fig. 8**) and based on the DIN concentrations it is oligotrophic to hypertrophic, even though concentrations of inorganic nutrients are known to be low in tropical mangrove waters within the µM range (Alongi et al. 1992). However, the criteria application should be treated with caution as the division into an oligotrophic, mesotrophic and eutrophic status should be made with total nitrogen and total phosphorus. The study by Jennerjahn et al. (2009a) and this thesis only used the inorganic dissolved nutrients as total N and P data were not available. However, it can be assumed that the total phosphorus and total nitrogen concentrations are higher than those for the inorganic dissolved nutrients. In the Piracicaba River, South Brazil, about two-thirds of the average total nitrogen export consisted mainly of DON followed by ammonium and nitrate (Filoso et al. 2003).

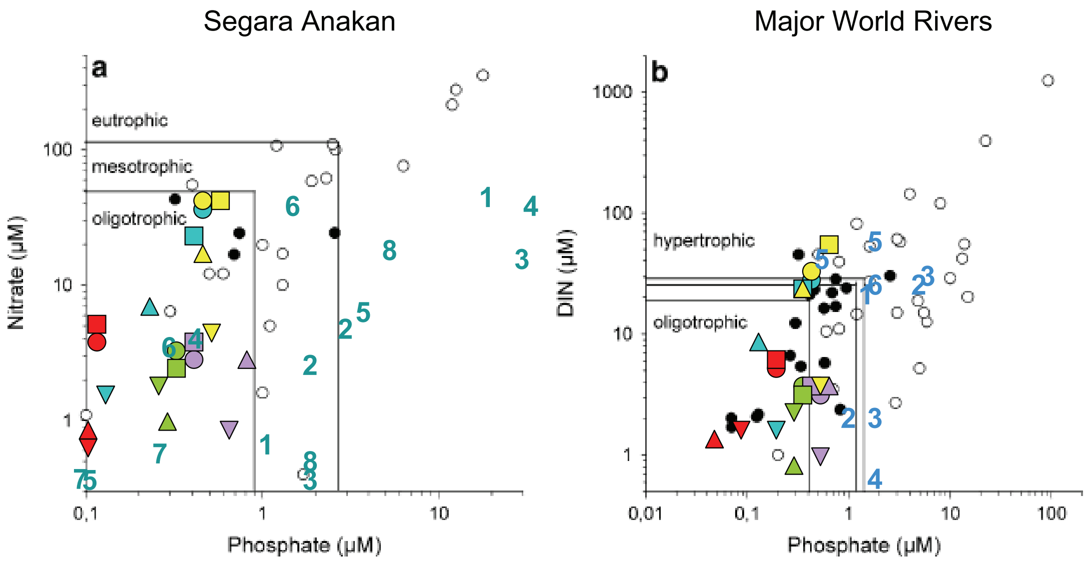

Fig. 8: The trophic state of the Segara Anakan Lagoon and major world rivers after the criteria of Smith et al. 2003. Red: Sept. 2007, blue: Feb. 2008, purple: Sept. 2008, yellow: Feb. 2009, green: Sept 2009; circle: Citanduy River, square: western area, triangle up: central area, triangle down: eastern area. Numbers indicate other tropical mangrove rivers, estuaries and lagoons. Green numbers (left): 1= Vatuwaga, Fiji (Nedwell 1975); 2= Kerala estuaries, India (Sarala et al. 1983), 3= West Malaysia (Nixon et al. 1984), 4= Phuket, Thailand (Limpsaichol 1984), 5= Kedah, Malaysia (Alongi et al. 1992 and references therein), 6= Porto Novo, India (Kannan & Krishnamurthy 1985), 7= Hinchinbrook Island, Australia (Boto & Wellington 1988), 8= Fly River, Papua New Guinea (Robertson et al. 1992). Blue numbers (right): 1= Chiko Lagoon (Hung & Kuo 2002), 2: Caeté Estuary dry and rainy season (Dittmar & Lara 2001b), 3: Caeté Estuary dry and rainy season (Lara & Dittmar 1999), 4: Paraiba do Sul River (Silva et al. 2001), 5: Celestun Lagoon, dry and rainy season (Herrera-Silveira 1996). The numbers occurring twice in one graph indicate upper and lower concentrations. Graphs modified after Jennerjahn et al. (2009).

However, it has been shown in **paper 2** that the DON concentration varied with season. Therefore, it is conceivable that the SAL rather ranges in higher trophical states. Even the highest nitrate concentrations in the SAL were still in an oligotrophic state but similar to those reported from the Vatuwaga estuary, Fiji. This estuary was denoted as eutrophicated and polluted probably due to both high nitrate and phosphate concentrations (Nedwell 1975). In addition, the application of these criteria should include chlorophyll a and the Secchi disk transparency. Due to the high turbidity in the lagoon the chlorophyll a values were not included for the trophic classification.

It has been shown in **paper 2** that a high nutrient load discharges through the Citanduy River into the western and the central lagoon. However, DOC concentrations were not discussed there as the focus was on the nutrient inventory. DOC fluxes play a critical role in terrestrial ecosystems (Schwendenmann & Veldkamp 2005). The DOC in mangrove systems derives mainly from mangrove detritus (Dittmar et al. 2001, **paper 1**). Its concentration did not correlate with tidal salinity variations in our study on tidal variations (**paper 2**). Former investigations have shown a clear tidal pattern in the DOC concentration being highest at low tide due to the seepage of DOC-enriched porewaters (Boto & Wellington 1988, Lara & Dittmar 1999, Dittmar & Lara 2001b, Bouillon et al. 2007b). However, no DOC flux was observed in the incubation experiment (unpublished data). Under natural conditions only little DOC export from mangrove sediments in Australia was calculated, whereas a DOC efflux of ~0.05 to 199 mmol m^{-2} d^{-1} was detected when the sediment was poisoned with mercury despite a high concentration gradient between the overlying and the interstitial water (Moriarty 1986, Stanley et al. 1987, Alongi et al. 1989, Boto et al. 1989, Robertson et al. 1992, Robertson & Phillips 1995). Average bacterial productivity in these surface mangrove and adjacent sediments ranged between 1.7 and 424.6 mmol C m^{-2} d^{-1} (Moriarty 1986, Alongi 1988a, b, Alongi et al. 1989, Boto et al. 1989). On average, 5 to 51% of the carbon requirements were provided for bacteria at the sediment surface due to this efflux.

Microbes on the sediment can not only diminish the DOC efflux from the sediment, they probably also remove high amounts of DOC leached from the mangrove leaves. Soil microbes consumed 85% of the leachate of maple in Canada within one day and the remaining 15% in the following three days in an experiment (Lock & Hynes 1976). It is conceivable, that either microbes consume most of the DOC or that the DOC is adsorbed to the sediment as has been shown in a study in Brazil (Schwendenmann & Veldkamp 2005). For these reasons benthic fluxes were low and recycling did not significantly contribute to the DOC inventory in the lagoon.

A high possible input of carbon from leaf leaching into the SAL has been shown in **paper 1**. Taken the average flux values of the eight species investigated in this thesis, a DOC flux of 2.13 mM m^{-2} d^{-1} can be calculated. Assuming a mangrove area of 9,000 ha this leads to an average DOC flux of $191*10^6$ mM d^{-1} for the entire lagoon. This shows a very high possible input of carbon into the SAL. However, these fluxes are only 2% of those in the Citanduy River during the rainy season. Again, no flux data are available for the dry season to estimate a DOC input from the leaves when the river discharge is low. During the rainy season 2008, the Citanduy River imported DOC whereas the western and eastern outlets showed a net export (**Tab. 4**). Combining the three study areas, a net export of $\sim 8.9*10^6$ mol d^{-1} during spring tide and a net import of $\sim 4.0*10^6$ mol d^{-1} during neap tide can be calculated. As more DOC is exported during the rainy season, I conclude that the difference is balanced by an uptake of CO_2 by the plant species present in the SAL. This carbon is stored in leaves and released as DOC after leaf fall (**paper 1**).

Tab. 4: Estimated daily fluxes of dissolved organic carbon in the SAL during rainy season [mol d^{-1}]. Negative values indicate a net export while positive values indicate a net import. Fluxes were calculated according to the formula presented in **paper 2**.

Tide	Citanduy River	Western outlet	Eastern outlet
Spring tide	$9.6*10^6$	$-15.4*10^6$	$-3.1*10^6$
Neap tide	$6.4*10^6$	$-2.3*10^6$	$-0.1*10^6$

The DOC concentrations showed high variations even within sampling areas of the SAL and were 312 µM during the dry season and 740 µM during the rainy season (**Fig. 9**). Higher values were reported for an estuary in southeastern Australia, the Brahmaputra, the Huanghe, the Siak, and the Lena (Spitzy & Leenheer 1988, Telang et al. 1988, Baum et al. 2007, Vink et al. 2007). In North Brazil the high annual average DOC values of 360 µM were related to porewater seepage at ebb tide (Lara & Dittmar 1999, Dittmar & Lara 2001b). Despite significant fluxes of DOC during tidal cycles (see 5.1.2) a small net export to adjacent waters has also been shown in other studies (Twilley 1985, Boto & Wellington 1988, Dittmar & Lara 2001b, Jennerjahn & Ittekkot 2002, Dittmar et al. 2006, Kristensen et al. 2008). Nevertheless, export rates increase with rainfall events (Dittmar et al. 2001). In the Siak River, Sumatra, the DOC concentration were higher during the rainy season (2195 µM) compared to the dry season (1866 µM) (Baum et al. 2007). However, in the SAL as well as in Brazil and in India the concentrations were slightly higher during the dry season. It has been concluded in the studies in Brazil and India that this is due to intense evaporation resulting in an increase of OM, the decomposition of POM, dilution of DOC through rainfall as well as an enhanced outwelling of DOC during the rainy season (Balasubramanian & Venugopalan 1984, Dittmar et al. 2001, Krüger et al. 2004). Especially the enhanced outwelling might be the main reason for the lower DOC concentrations during the rainy season as shown by the much shorter residence time of the water.

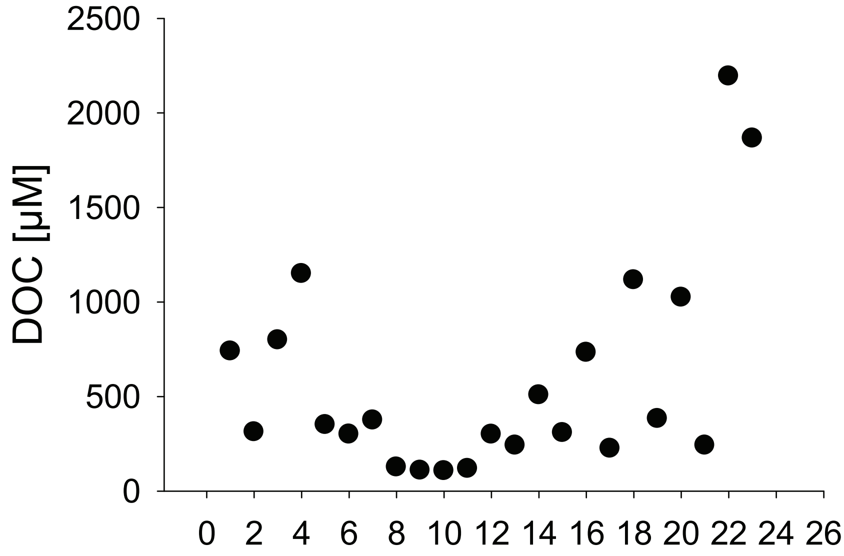

Fig. 9: DOC concentrations in the SAL, other mangrove fringed estuaries and lagoons and in major world rivers. 1= SAL (dry season), 2= SAL (rainy season), 3-4= Australia (Vink et al. 2007), 5-7= North Brazil (Lara & Dittmar 1999, Dittmar & Lara 2001b), 8-10= East Brazil (Ovalle et al. 1999), 11-18= Amazon, Orinoco, Uruguay, Mississippi, Yangtsekiang, Brahmaputra, Ganges and Huanghe (Spitzy & Leenheer 1988), 19= Niger (Martins & Probst 1988), 20-21= Lena and Yenisei (Telang et al. 1988) 22-23= Siak (rainy and dry season) (Baum et al. 2007).

POM in the water column can derive from living organisms like phytoplankton, bacteria and animals and non-living particles such as detritus (Eisma & Cadeé 1988). It has been shown in **paper 3** that most of the suspended matter in the western lagoon derived from the rice fields in the hinterland whereas in the eastern lagoon mainly from mangrove leaves. At the western outlet ~$15.4*10^6$ mg l^{-1} d^{-1} is exported to the Indian Ocean (Santoso pers. comm.). However, only little input from the Ocean was observed despite high salinities. In **paper 2** it was stated that the eastern lagoon is indirectly affected by the Serayu River whose freshwater and nutrients is flushed through Penyu Bay into the lagoon. Also this river seems to contain high loads of TSM (**Fig. 10**) even though this was not quantified in the current thesis. It is unclear whether also suspended matter from the Serayu River enters the eastern lagoon. As the TSM load in the eastern area was low with ~24 mg l^{-1} during the rainy season 2009 it is rather unlikely that the Serayu River affects the suspended matter in the SAL. However, estimated daily flux rates of POC during the rainy season 2008/2009 indicated a net import of TSM during spring tide at the eastern outlet with $0.3*10^6$ mg l^{-1} d^{-1} while a net export of $0.1*10^6$ mg l^{-1} d^{-1} was observed during neap tide (Santoso pers. comm.).

Fig. 10: The SAL and the Citanduy River in the western lagoon and the Serayu River which discharges water into Penyu Bay (image from 1996, source unknown).

The lagoon area decreased about 55% between 1987 and 2006 (Ardli & Wolff 2009). The water depth in the central area averaged between 0.3 m in the dry season and 1.3 m in the rainy season from 2007 to 2009 and was deepest at the eastern outlet with up to 13.4 m during the rainy season (unpublished data). Flux calculations during the rainy season 2008/2009 revealed that ~80% of the TSM from the Citanduy River settles in the lagoon during spring tide and < 15% during neap tide (Santoso pers. comm.). However, this rate is likely to be overestimated and is not representative for the whole year. It has already been predicted that the lagoon will disappear until the 1990´s which was tried to prevent by dredging. As the lagoon did not disappear within the 1980 it has been estimated that the SAL would be closed by the year 2025 though, it is more likely that a small and stable residual lagoon will remain (Turner 1985).

4.2 Global relevance of this thesis

As mentioned earlier mangrove studies are rare. The findings presented here are also relevant for other mangrove ecosystems. Many studies with global budget estimations concentrated on leaf production and litterfall but did not take into account processes like leaf leaching (**paper 1** and **4**) and consumption by crabs. The determination and quantification of nutrient and DOC sources like mangrove and shrub species are therefore highly important to improve future global estimates of nutrient and DOC export rates to coastal zones. Many studies on mangrove ecosystems with regard to nutrient concentrations and fluxes showed high variability in their data sets but most of them were either related to seasonality or to tidal variations. However, it has been shown in **paper 2** that it is important to determine both factors as well as associated processes like benthic recycling. Also in the current thesis only small-scale variabilities were investigated and not all the gaps in knowledge can be filled with these results. However, the findings presented here will improve the understanding of biogeochemical processes in mangroves worldwide and will also be important for global budget calculations. With five years of investigation the SAL belongs, besides

Hinchinbrook Island, Australia, and the Caeté estuary, Brazil, to one of the best studied mangrove ecosystems in the world.

4.3 Consequences of a shift in the vegetation structure and implications for management in the SAL

The consequences of logging can not totally be predicted with the results shown in this thesis. It has been explained in **paper 1** and **4** that a shift in vegetation from mangrove tree species to the shrub species *Acanthus* and *Derris* might lead to a changing nutrient inventory of the lagoon. Taken the calculations from **Tab. 3** but divided into mangrove tree species (average DOC flux of $146*10^6$, a PO_4^{3-} flux of $27*10^6$, a DIN flux of $114*10^6$ and a $Si(OH)_4^-$ flux of $3*10^9$ µM d^{-1}) and *Acanthus ilicifolius* and *Derris trifoliata* (average DOC: $327*10^6$ µM d^{-1}; PO_4^{3-}: $42*10^6$ µM d^{-1}; DIN: $282*10^6$ µM d^{-1} and $Si(OH)_4^-$: $5*10^9$ µM d^{-1}) the fluxes of the shrub species are between 1.6 and 2.2 times higher than for tree species. However, an impact of these changes on the nutrient inventory can not be estimated. So far the effects of a higher shrub abundance on the nutrient inventory in the SAL are unclear. As shown in **paper 2** no trend in the nutrient concentration over the five years of investigation was observed even though it is likely that the abundance of *Acanthus* and *Derris* increased during this period. However, a period of five years might not be sufficient to determine the changes in the vegetation structure with regard to nutrient availability. Even though an increase in the nutrient concentration in the lagoon is rather unlikely due to the short residence time of the water (Holtermann et al. 2009) as well as consumption of leaves by micro- and macroorganisms, the possible effects of an increasing nutrient concentration will be briefly demonstrated. Assuming the nutrient concentration will increase due to an increase in the number of villages (pers.

observation). This could result in a greater investment in the leaves, e.g. leaf area, number of leaves and leaf area ratio (McKee 1995, Kaye & Hart 1997, Hogarth 2007 and references therein) as well as in an alteration of the chemical composition of leaves (Vitousek 1982, McKee 1995, Feller et al. 2003). This, in turn, could affect the whole food web. If the nutrient input into the SAL increases it is likely that the outwelling of nutrients to the coastal zone also increases. This might disrupt the balance between the production and metabolism of OM in the coastal zone and might change the abundance and species composition of phytoplankton to e.g. toxic algae and therefore of the whole food web (Cloern 2001, Smith 2003, Howarth & Marino 2006, Seitzinger et al. 2010).

The information developed in this study in combination with other research in the SPICE program is useful in developing strategies for management and conservation of the natural resources of the SAL. The lagoon is endangered by various threats, especially logging of wood. It has been stated earlier that management programs failed in the past decades in the SAL (Yuwono et al. 2007a). This thesis has been shown that the consequences of a shift in the vegetation structure, e.g. due to intensive tree logging, can not be foreseen. However, cutting will affect not only the tree diversity, it will have an impact on the whole food web and therefore also for the indigenous people. It has been shown in Timor Leste that small-scale logging can lead to a decline of the leaf area index of mangrove leaves and to an increase of dissolved sulphide, metals and ammonium due to enhanced soil desiccation and therefore an increase in salinity. This, in turn, can cause a decline in oxygen (Alongi & Carvalho 2008). In addition, due to the gap creation, soil erosion, changes in canopy microclimate, loss of associated fauna and flora and their biodiversity and alterations in the hydrology and biogeochemistry can occur (Bruijnzeel 2004). It has been shown that the free space after logging is invaded by the shrub species *Acanthus ilicifolius* and *Derris trifoliata* so that a natural regeneration of mangrove trees in the SAL is unlikely even though high numbers of pneumatophores were observed (pers. observation). It is highly important that new management strategies are established considering the interests of the different stakeholders as well as a balanced ecosystem. Such strategies should also incorporate sustainable harvest of mangrove forest as shown for management implications in Timor Leste (Alongi & Carvalho 2008). In a study in a mangrove forest in western Venezuela the ecological definition of sustainable harvesting was “harvesting that allows the mangrove population to be maintained or to increase over time” even though different stakeholders had a different definitions of sustainable harvest (López-Hoffman et al. 2006).

A complete prohibition of mangrove harvesting has been proven to be ineffective and generated social problems like in North Brazil where cutting by local people is commonplace (Glaser et al. 2003). It has been recommended in other studies that a community-based management is a good approach (Glaser et al. 2003, Omodei Zorini et al. 2004, Walters 2005, López-Hoffman et al. 2006, Alongi & Carvalho 2008). Most of the cutting in the SAL seems to be rather for private consumption than for industries. The inhabitants of the lagoon have realized the consequences of logging but due to their private needs they will continue due to a lack of any alternatives. A community-based management approach by involving families of the local villages might have a fair chance to succeed as in some areas villagers already participate voluntarily in reforestation projects (Hermawan. pers. comm.).

5. Conclusion

A summary of the topics addressed in this thesis is given in **Fig. 11**.

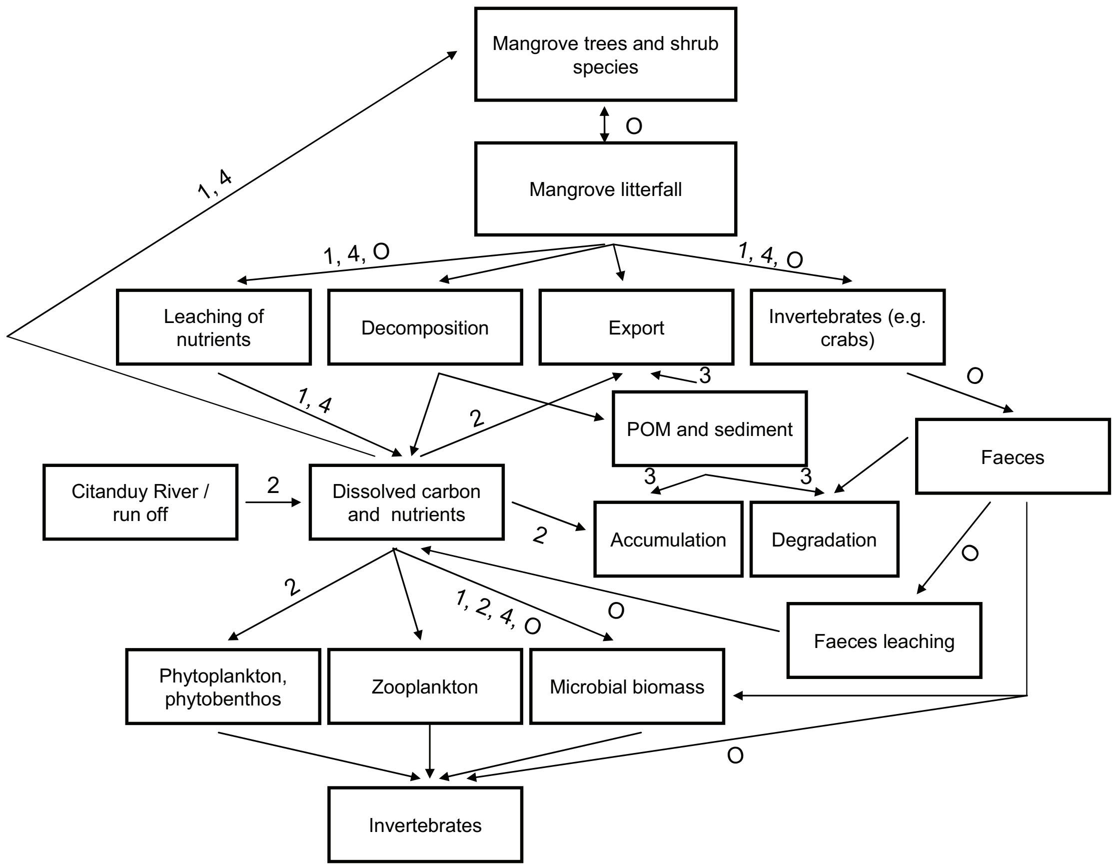

Fig. 11: The topics and interactions addressed in the current thesis (1-4= paper numbers, O= outlook).

1) **What are the sources and sinks of nutrients and organic carbon and what are their spatial and temporal variations?**

The main sources of nutrients and DOC in the SAL are the input of the Citanduy River and therefore from the agriculture-dominated hinterland as well as mangrove leaves. The nutrients brought into the lagoon are consumed by microbes, mangrove and shrub species as well as to a lesser extent by phytoplankton and phytobenthos. Another sink for nutrients and DOC is the short residence time of the water and therefore outwelling. The hydrology of the SAL is driven by tidal variation as well as the freshwater input from the rivers. However, the river discharge and therefore the nutrient input changes with seasons.

2) **Which patterns influence the sedimentation of the SAL and what is the origin of the sediment?**

Most of the suspended matter in the SAL derives from terrestrial plants like mangrove species and rice plants but not from marine sources. The distribution of TSM is driven by tidal variations and river discharge which changes between the seasons. The organic material of this suspended matter accumulates in the lagoon and undergoes substantial degradation or is exported to the Indian Ocean.

3) **What might be the impact of a change in the vegetation structure on the carbon and nutrient inventory in the lagoon?**

Due to logging a shift in the vegetation in the SAL occurred already in the last 25 years. Nowadays the shrub species *Acanthus ilicifolius* and *Derris trifoliata* dominate the mangrove community. A shift in vegetation due to logging might lead to an increase in the DOC inventory and element cycling in the lagoon. This, in turn, could promote microbial activity and lead to shifts in food web structures as not all benthic organisms feed on leaves of the shrub species.

6. Outlook

In former studies the carbon and nutrient contributions by mangroves to the coastal ecosystems and the open ocean were estimated on a global scale but only a few parameters like the litter production and litterfall were used (Jennerjahn & Ittekkot 2002, Dittmar et al. 2006). To reduce the high number of uncertainties in such global estimates it is necessary to understand more of the factors that might influence the export rates. A summary of open questions is presented in **Fig. 12**.

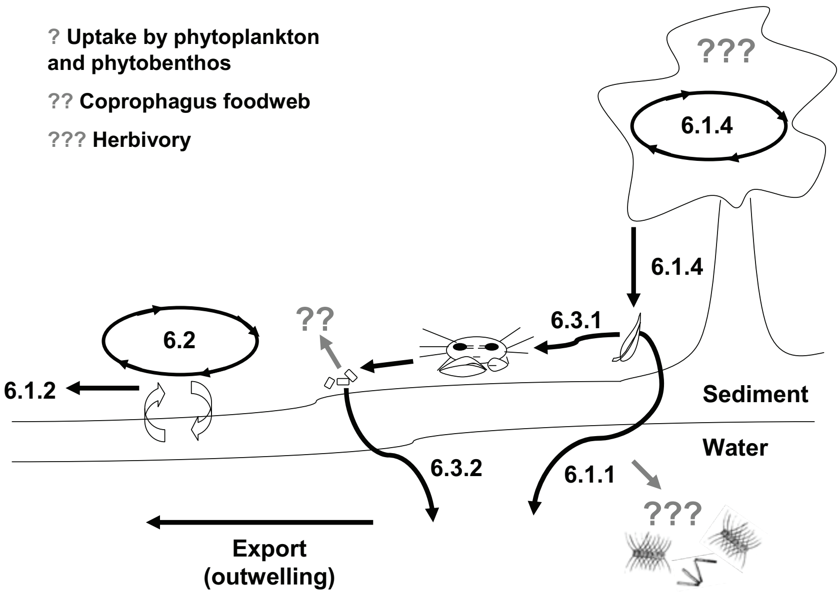

Fig. 12: Summary of open questions. Numbers in the figure correspond to the numbering in the outlook.

6.1 Mangrove trees and leaves

<u>6.1.1 Leaching experiments:</u> The following factors should be included in future leaching experiments including the other three abundant species *Avicennia alba, Rhizophora mucronata* and *Sonneratia alba* as an influence has been shown in former studies on single mangrove or other tree species:

- Presence of microbes and fungi (tested by poisoned and unpoisoned samples) (Lock & Hynes 1976, Maie et al. 2006).
- Leaf size / leaf conditions: fragmented (cut) leaves to simulate the presence of crabs (Harrison & Mann 1975, Skov & Hartnoll 2002).
- Throughfall: leaching already begins while leaves are still attached to the trees but are exposed to rainfall as has been shown in an experiment with pine needles (Kowal 1969) and sugar maple (McClaugherty 1983) as well as in a tropical wet forest in Costa Rica (Schwendenmann & Veldkamp 2005). It is conceivable that this process is also important for the SAL during November until March when the wet monsoon brings heavy precipitation.

It is also necessary to investigate the leaching rate of other tree parts like roots and wooden parts (twigs, branches, bark) (Van der Valk & Attiwill 1984, Robertson & Daniel 1989a), propagules (Albright 1976) as well as the leaf sinking rates (Schories et al. 2003). *Rhizophora* and *Sonneratia* are buoyant and can float for several days before they sink, whereas *Avicennia* leaves sink immediately (Wafar et al. 1997).

6.1.2 Bacteria and microbes: It has been assumed that microbes can consume significant amounts of DOC (**paper 1**) and nutrients (**paper 2** and **4**). In calculating the carbon turnover within a mangrove forest the degree of litter decomposition by microbes is an important factor (Robertson 1986, Twilley et al. 1986) but studies providing reasonably accurate estimates of bacterial densities in mangrove sediments or on litter are rare (Alongi & Sasekumar 1992). Therefore, the bacterial biomass should be investigated in the SAL.

6.1.3 Litterfall: Essential for the budget calculations will be the litterfall rates and litter standing stocks on the sediment. The litterfall and standing stock was investigated by the Master student Angela Maria Oviedo in this area in 2009. Due to a loss of most litter fall traps this needs to be repeated both during rainy and dry season as species show inter annual differences in litterfall (Dehairs et al. 2000, Priabdi 2003).

6.1.4 Nutrient use efficiency (NUE): The NUE is an important ecological measure. It is an estimate of the productivity per unit nutrient uptake or loss (Alongi et al. 2005). A number of studies showed that mangrove ecosystems are highly efficient at conserving nutrients in oligotrophic waters and that the NUE is species dependent (Lovelock & Feller 2003, Alongi et al. 2005).

6.2 Benthic recycling

Benthic flux experiments in North Queensland, Australia, as well as in the SAL have shown that there is only little export of DOC and nutrients from mangrove sediments probably due to an uptake by microorganisms (Alongi et al. 1989, Robertson et al. 1992, **paper 2**). Therefore, the consumption rate of nutrients deriving from porewaters by microbes needs to be investigated by a comparison between poisoned and unpoisoned chambers. Furthermore, many studies have reported seasonal differences in nutrient fluxes (Boynton & Kemp 1985, Billen et al. 1989, Cowan & Boynton 1996, Friedrich et al. 2002) while others did not like at Hinchinbrook Island (Alongi 1996). Therefore, further investigations on the recycling processes in the SAL during the rainy season are required as our results are not quantitative for the whole year.

6.3 Food preference of crabs and leaching rates of crab faeces

6.3.1 Leaf consumption by crabs: Mangrove-derived detritus is known to be an important food source for decomposer food webs. Some crab species are capable of removing up to 90% of litterfall (Robertson 1986, Robertson & Daniel 1989b, Bouillon et al. 2002, Schories et al. 2003, Kristensen & Alongi 2006, Kristensen et al. 2008). It has been shown in a 24 h experiment in the SAL by C. Herbon that the three dominant leaf-eating crabs *Episesarma versicolor, Episesarma singaporense* and *Perisesarma darwinense* preferably consume *R. apiculata* and *D. trifoliata* leaves whereas *A. ilicifolius* and *A. corniculatum* leaves were not eaten at all. To follow the fate of leaves from falling to decomposition the consumption of crabs is an important factor influencing the input of DOC and nutrients into the lagoon. Therefore, these experiments need to be conducted also with other abundant leaf-eating crabs which should also be offered other dominant leaf species like *Bruguiera gymnorrhiza, Ceriops tagal*, *Rhizophora mucronata, Sonneratia caseolaris* and *S. alba* as well as mangrove propagules. Especially grapsid crabs can greatly effect natural regeneration and influence the distribution of certain species across the intertidal zone by consuming high amounts of propagules (Smith III 1992 and references therein). Additionally, the faeces production rate should be measured.

<u>6.3.2 Faeces leaching:</u> It has been shown in a preliminary experiment with two abundant crab species that the faeces of crabs fed exclusively on *Rhizophora apiculata* leaves still leach ~10% of the leaf itself. In *Bruguiera* forest, sesarmid crabs can produce ~260 g C m^{-2} y^{-1} of litter-derived faeces, which corresponds to ~70% of bacterial production (Robertson & Daniel 1989b). Former studies on fish faeces showed that leaching of faeces can have a significant input of nutrients to the water column (Lee 1997). Even if the leaching of faeces might be much lower compared to the senescent leaves the high crab abundance and therefore the probably high production of faeces in the SAL can also contribute significantly to the DOC and

nutrient pool in the lagoon. Therefore, it is necessary to conduct this experiment with other abundant crab species which are fed with different mangrove leaves.

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8. Appendix

Paper 1: Leaf leaching of dissolved organic carbon from eight plant species in the mangrove-fringed Segara Anakan Lagoon, Java, Indonesia

Author's contribution:

Regine Moll:	Sampling, sample preparation, preparation of figures and tables, preparation of main manuscript
Janina Korting:	Sample analysis, data discussion and manuscript review
Angela M. Oviedo:	Sampling, sample analysis
Tim Jennerjahn:	Data discussion and manuscript review

Journal: Marine Ecology Progress Series

Current status: Under review

Paper 2: Nutrient dynamics in the Segara Anakan Lagoon, Java, Indonesia

Author's contribution:

Regine Moll:	Sampling, sample preparation, preparation of figures and tables, preparation of main manuscript
Arianto B. Santoso:	Sample analysis, investigation of tidal cycles, data discussion and manuscript review
Tim Jennerjahn:	Data discussion and manuscript review

Journal: Estuarine, Coastal and Shelf Science

Current status: Under review

Paper 3: Fate of organic matter derived from mangroves and from an agriculture-dominated hinterland in the Segara Anakan Lagoon, Java, Indonesia

Author's contribution:

Regine Moll: Sampling, sample preparation, preparation of figures and tables, preparation of main manuscript

Tim Jennerjahn: Data discussion and manuscript review

Journal: Journal of Sea Research

Current status: In preparation

Paper 4: Leaching of dissolved inorganic nutrients from eight mangrove and shrub species in the Segara Anakan Lagoon, Java, Indonesia

Author's contribution:

Regine Moll: Sampling, sample preparation, preparation of figures and tables, preparation of main manuscript

Janina Korting: Sample analysis, data discussion and manuscript review

Tim Jennerjahn: Data discussion and manuscript review

Journal: Marine Ecology Progress Series (as a note)

Current status: Under review

Leaf leaching of dissolved organic carbon from eight plant species in the mangrove-fringed Segara Anakan Lagoon, Java, Indonesia

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Abstract

Leaching experiments with eight plant species were performed in the mangrove fringed Segara Anakan Lagoon, Java, Indonesia. The leaching rates of dissolved organic carbon (DOC) and leaf weight loss rates were determined at salinity concentrations of 0, 10, 20 and 30 psu over a period of 30 days for *Acanthus ilicifolius, Aegiceras corniculatum, Avicennia marina, Bruguiera gymnorrhiza, Ceriops tagal, Derris trifoliata, Rhizophora apiculata* and *Sonneratia caseolaris*. Salinity had little influence on the leaching. Only for *A. corniculatum* and *S. caseolaris* DOC concentrations were higher in freshwater than in saline water. Highest DOC concentrations were detected for *A. ilicifolius* and *A. marina* with up to 115.1 and 53.6 mM g^{-1} dry weight, respectively, and lowest for *B. gymnorrhiza* with up to 4.1 mM g^{-1} dry weight. A decrease in the DOC concentrations for all species except for *B. gymnorrhiza* was observed after between seven and 15 days of the experiment. Large species-specific variations were observed and leaching

concentrations differed by more than one order of magnitude. *A. corniculatum, Nypa fructicans* and *R. apiculata* were dominant tree species in the eastern part of the lagoon, whereas *Avicennia alba, A. corniculatum* and *S. caseolaris* dominated the central part. The vegetation changed within the last 25 years due to logging, so that today in most areas the shrub *A. ilicifolius* dominate the plant community. A shift in vegetation due to logging might lead to an increase in the DOC inventory and element cycling in the lagoon. This, in turn, could promote microbial activity and lead to shifts in food web structures.

Keywords: Mangrove leaves, leaching, dissolved organic carbon, Segara Anakan Lagoon

1. Introduction

1.1 Mangroves

Mangroves, which are highly productive ecosystems, represent nearly 75% of the world's tropical and subtropical coastline with an estimated area of 1.7×10^5 km^2 (Odum & Heald 1975, Duarte & Cebrián 1996, Valiela et al. 2001, Marchand et al. 2006), but decline at a rate of 2% per year (Valiela et al. 2001). Coastal ecosystems like mangroves link the carbon cycles of land and ocean (Dittmar et al. 2006). Mangrove vegetation is important in contributing organic matter to its associate fauna and sediment as well as to the adjacent ecosystems due to tidal exchanges (Odum & Heald 1975, Basak et al. 1998, Jennerjahn & Ittekkot 2002, Dittmar et al. 2006). Outwelling transports the terrigenous organic matter to the ocean. It was estimated that >10% of the terrestrial-derived DOC in the ocean comes from mangroves, even though they cover <0.1% of the continents` surface (Dittmar et al. 2006). Leaching from peat swamps can also be an important DOC source as has been shown for the Siak River and its tributaries on Sumatra, Indonesia (Baum et al. 2007, Rixen et al. 2008).

Mangrove plant litter composes about 30 to 60% (Duarte & Cebrián 1996) of the total production. Typical global average litter fall rates are on the order of ~38 mol C m^{-2} yr^{-1} (Jennerjahn & Ittekkot 2002). About half of the produced mangrove plant litter is exported to adjacent coastal waters (Robertson et al. 1992, Duarte & Cebrián 1996, Dittmar & Lara 2001a, Jennerjahn & Ittekkot 2002). This detrital material serves as the base for food webs in estuarine and coastal environments (Odum & Heald 1975, Rodelli et al. 1984, Alongi et al. 1989) whereof 40% of the carbon produced is decomposed and recycled within the system, 30% is exported, 10% is stored in sediments and 9% is consumed by herbivores (Duarte & Cebrián 1996).

1.2 Leaching

The decomposition of leaves can contribute a significant amount of organic matter to the marine food web in tropical and subtropical regions (Cundell et al. 1979, Jennerjahn & Ittekkot 2002). Leaf breakdown consists of four major steps: animal feeding, microbial activity, physical fragmentation and leaching (Stewart & Davies 1989). An important early phase in decomposition of leaf material is the leaching of water soluble compounds (Cundell et al. 1979, Robertson 1988, Chale 1993). Via leaching a leaf can lose around 30 to 50% of its organic matter (Cundell et al. 1979, Newell et al. 1984, Robertson 1988, Davis III et al. 2003). The leaf material loss caused by leaching varies with leaf species as shown for trees like alder, birch and maple (Lush & Hynes 1973, France et al. 1997) and environmental settings (Robertson et al. 1992). The loss varies from 14 to 40% of the initial dry weight (Van der Valk & Attiwill 1984, Camilleri & Ribi 1986, Steinke et al. 1993). While the complete decomposition of a leaf can take months or even years, the leaching process typically lasts from a few days to a few weeks (Cundell et al. 1979, Steinke et al. 1993, Davis III et al. 2003). Former studies have shown the influence of salinity on the leaf leaching process. For example the leaching of DOC from senescent leaves of deciduous trees like hickory and maple was faster in freshwater than in marine environments (Lush & Hynes 1973), or that there was a significantly greater decrease in the dry mass of *Avicennia marina* in water at 16‰ than of 32‰ (Steinke et al. 1993) suggesting that leaching decreases at an increasing amount of salt ions.

Heterotrophic decomposition of the remaining particulate organic matter (POM) by bacteria and fungi is important (Steinke et al. 1990, Robertson et al. 1992) and can increase the absolute nitrogen content of the leaf litter (Rice & Tenore 1981). POM can either be utilized as a food source by fauna like crabs (Malley 1978, Robertson 1986, Kristensen & Alongi 2006), or be colonized by bacteria and fungi which live on plant tissue. By metabolizing mangrove OM and converting it into their own biomass these microorganisms make nutrients available to higher trophic levels (Harrison & Mann 1975, Rodelli et al. 1984). Herbivorous crabs store mangrove leaves in their burrows before consumption where the amount of colonizing fungi can increase (Nordhaus & Wolff 2007). The leached DOC can precipitate as particles, so that it becomes available to other organisms. Microorganisms attached to dead leaves can either feed on these particles or on the DOC directly (Murray & Hodson 1985, Benner et al. 1986, Camilleri & Ribi 1986).

Many studies on leaf leaching (or leaf decomposition in general) used the litter bag technique to obtain information on the remaining part of the leaf after leaching occurred (Newell et al. 1984, Van der Valk & Attiwill 1984, Robertson 1986, Twilley et al. 1986, Mackey & Smail 1996, Wafar et al. 1997). Yet little attention has been paid to the solubles leached out of leaves. Most of these studies focussed on single mangrove species not taking into account possible species-specific variations in the leaching (Benner et al. 1986, Steinke et al. 1993, Davis III et al. 2003, Maie et al. 2006). Here we present the results of a leaf leaching experiment using eight plant species from the Segara Anakan Lagoon (SAL). This study provides information on the DOC leached out of leaves from eight abundant mangrove and shrub species in the Segara Anakan Lagoon. The influence of salinity differences on the leaching process was also investigated.

We hypothesize a) that the salinity has a significant effect on the concentration and leaching rate of DOC from the leaves and b) that the DOC concentrations leached from leaves differs between species.

2. Material and Methods

2.1 Study area

The Segara Anakan Lagoon (108°46′E – 109°03′E, 7°35′S – 7°48′S; Fig. 1) is the largest remaining mangrove stand on the south coast of Java with >9000 ha in 2006 (Ardli & Wolff 2009). The hydrology of the lagoon is governed by a seasonally varying river runoff of the Citanduy River in the West and tidal exchange with the

Indian Ocean through two channels in the eastern and western part of the lagoon (White et al. 1989, Yuwono et al. 2007). These factors are responsible for the varying salinity and the suspended sediment load of Segara Anakan. A rising water level during flood pushes the water from the Citanduy into the lagoon and can therefore cause a strong decrease in salinity in the whole lagoon. Mean salinity during dry season is 29 to 33. In the central part of the lagoon, the salinity decreased from a range of 14-19 to about 9 during rainy season in the last 25 years (Holtermann et al. 2009).

Insert Fig. 1

In the SAL 21 mangrove tree species and five understorey genera occur with tree densities of 0.80 (± 0.99) Ind/m^2. *Aegiceras corniculatum, Nypa fructicans* and *Rhizophora apiculata* are the dominant species in the eastern part of the lagoon, whereas understorey and pioneer species such as *Avicennia alba, Aegiceras corniculatum* and *Sonneratia caseolaris* as well as the genera *Bruguiera* and *Rhizophora* dominate the central part (White et al. 1989, Hinrichs et al. 2009). Besides true mangrove species the vine *Derris* and the shrub *Acanthus* are abundant in the SAL (Hinrichs et al. 2009). These plants generally occur in mangrove ecosystems with natural and human disturbances since gaps, e.g. due to logging, are rapidly occupied by them (Hogarth 2007). As these two species prefer habitats of low salinity (Joshi & Ghose 2003, Ye et al. 2005) they have higher abundances in the central than in the eastern part of the lagoon (White et al. 1989).

2.2 Sampling and experimental design

During September and October 2009 one water sample each was taken at 22 stations in the lagoon (one in the Citanduy, five in the western area [area W], seven in the central area [area C] and nine in the eastern area [area E], Fig. 1). 10 ml of surface water for DOC analysis was filtered through syringe filters (pore size 0.45 µm) into pre-annealed glass ampoules and treated with 1M hydrochloric acid. The ampoules were sealed and stored dark and cool until measurement. DOC samples were combusted in a Teledyne Tekmar Apollo 9000 Combustion TOC analyzer at 680 °C.

A leaf leaching experiment was conducted with leaves from the six mangrove species *Aegiceras corniculatum, Avicennia marina, Bruguiera gymnorrhiza, Ceriops tagal, Rhizophora apiculata* and *Sonneratia caseolaris* as well as with leaves from the shrub species *Acanthus ilicifolius* and *Derris trifoliata*. Yellow senescent leaves were hand-picked from the plants. The leaves collected were symmetrical and without damages, except for *A. marina* leaves which often had insect grub areas.

Each leaf was weighed before the start of the experiment. One leaf at a time was submerged in glasses containing 400 ml of artificial sea water at four salinities: 0, 10, 20 and 30 g l^{-1}. *A. corniculatum* and *A. ilicifolius* leaves were additionally used for an experimental approach with lagoon water (22.1 psu) to simulate leaching under natural conditions. This approach could only be conducted for these two species. Leaves were removed from the glasses at eight times (10 sec, 2 h, 6 h, 1 d, 3 d, 7 d, 15 d, 30 d). For each experimental approach three replicates were prepared. After removing the leaves, they were dried at 40 °C and weighed again. The weight loss for each leaf at each sampling point was calculated with the following equation:

$$WL = WLi[\%] - WLtx[\%]$$

Where WL= weight loss, i= initial leaves which were not used for the incubation experiment, t= weight loss at time x. The water was stirred and 10 ml of water sample was taken (treatment see above).

2.3 Data analysis and calculations

The concentration of DOC was calculated in mM g^{-1} dry weight (dw) and fluxes as mM g^{-1} dw d^{-1}. Differences between the four salinities, sampling times and species were tested with a three-way ANOVA using STATISTICA 9. Because of highly variable standard deviations the p-values were calculated by a simulation after (Westfall & Young 1993). Test decisions base on a critical significance level (p-value) of 5%.

The data of seven species showed a peak in DOC concentration. As sampling intervals were long at the end of the experiment it is likely that the maximum concentrations measured was not the maximum release of DOC. Therefore a non-linear regression was calculated to identify the point in time, when DOC concentrations reached a maximum using the following formula:

$$\log DOC = a * \exp(b * time) + c(1 - \exp(d * time))$$

where *a* is a measure of the total DOC increase, *b* is a coefficient for the speed of increase, *c* is a measure for the total DOC decrease and *d* is a coefficient for the speed of decrease. Parameters were estimated by iterative fitting using the Marquard-Levenberg method (Marquardt 1963). The logarithm was used to obtain a constant error distribution over the whole data set.

For *A. marina* the maximum concentration can not be calculated by an explicit equation as these data did not follow the fitting. Therefore the curvature term *e* was included:

$$\log DOC = a * \exp(b * time) + (e * time^2) + c(1 - \exp(d * time))$$

Although only two data points could be used for this term the resulting equation properly reproduces the measured data points.

3. Results

3.1 DOC concentrations of leaching experiments

No significant differences were found between the amount of leached DOC in the four salinity treatments for most of the species (Tab. 1 and Fig. 2). Even though most species showed higher DOC concentrations in distilled water, the difference between fresh and saline water was only significant for *Acanthus ilicifolius* and *Sonneratia caseolaris* at the last one or two sampling points (AC $p= 0.01$; SC $p= 0.02$). No differences were found between all sampling times for *A. ilicifolius* between lagoon water (22.1 psu) and the artificial sea water at 20 g l^{-1} ($p = 0.89$), whereas *Aegiceras corniculatum* showed significant differences ($p= 0.03$) (Fig. 3), but these differences were due to both higher and lower DOC values of the artificial sea water compared to lagoon water at different sampling times, so that this significant difference is rather due to the high variability in the data.

Highest concentrations were found in *A. ilicifolius* with up to 115.1 ± 71.5 mM g^{-1} dw after 7 d, followed by *Avicennia marina* with up to 53.6 ± 27.9 mM g^{-1} dw after 15 d. The statistically significant lowest concentrations of the eight species were determined for *Bruguiera gymnorrhiza* with up to 4.2 ± 2.4 mM g^{-1} dw after 30 d. Significant differences were found between the eight species ($p < 0.01$). No differences were found between *A. corniculatum, Ceriops tagal, Rhizophora apiculata* and *S. caseolaris*.

Insert Fig. 2

Insert Fig. 3

3.2 DOC concentration in the lagoon

In all three areas of the lagoon similar DOC concentrations were found with average values of 0.20 ± 0.08 mM (Area W), 0.22 ± 0.03 mM (Area C) and 0.24 ± 0.10 mM (Area E) (Fig. 4). A much higher concentration (1.16 mM) was measured in the Citanduy River.

Insert Fig. 4

3.3 Calculation of maximum DOC release

As DOC concentrations leached from leaves of all species decreased after some time, except for *Bruguiera gymnorrhiza,* a non-linear regression was used to identify the point in time when the DOC concentration in the water was highest. The estimated parameters for the seven species are presented in Tab. 2.

Insert Tab. 2

Maximum DOC concentrations for *Acanthus ilicifolius, Rhizophora apiculata* and *Sonneratia caseolaris* were measured between 6 – 14 d (Fig. 5). Afterwards the concentrations decreased. Latest maxima were observed for *Aegiceras corniculatum, Avicennia marina* and *Derris trifoliata* after more than 13 d. We assume that until the maximum DOC concentration was measured, the amount of DOC leached was higher than the amount of DOC consumed by microbes or fungi. These could have been brought into the experiment on the leaves themselves as they were not cleaned before the experiment.

Insert Fig. 5

3.4 DOC fluxes

The fluxes were calculated with the average DOC concentrations of the four salinities. Highest fluxes for all eight species were found during the first 3 d. *Derris trifoliata* (78.8 ± 60.5 mM g^{-1} dw d^{-1} after 2 h), *Acanthus ilicifolius* (34.5 ± 43.8 mM g^{-1} dw d^{-1} after 1 d) and *Avicennia marina* (46.2 ± 15.2 mM g^{-1} dw d^{-1} after 2 h) had the highest DOC fluxes. *Bruguiera gymnorrhiza* and *Rhizophora apiculata* had the lowest fluxes with 1.3 ± 1.0 mM g^{-1} dw d^{-1} after 2 h and 3.8 ± 1.3 mM g^{-1} dw d^{-1} after 2 h.

4. Discussion

4.1 Factors controlling leaching

4.1.1 Time

Leaching can have a significant effect on the loss of the initial dry weight of leaves as shown from various litterbag studies (Van der Valk & Attiwill 1984, Camilleri & Ribi 1986, Robertson 1988). After 30 d the weight loss of *Aegiceras corniculatum, Avicennia marina, Bruguiera gymnorrhiza, Ceriops tagal, Derris trifoliata, Rhizophora apiculata* and *Sonneratia caseolaris* ranged between 11 and 40% which is similar to the range of 14 to 40% reported for litterbag studies (Van der Valk & Attiwill 1984, Camilleri & Ribi 1986, Steinke et al. 1993), but was higher in *Acanthus ilicifolius* leaves with 65% (Tab. 3).

Insert Tab. 3

The highest DOC fluxes occurred during the first hours and days of leaf submergence. Yule and Gomez (2009) also reported a fast leaching of DOC in the beginning of leaf breakdown, especially of carbohydrates and tannins. The flux of *R. apiculata* was highest after 2 h with 3.8 ± 1.3 mM g^{-1} dw d^{-1} and decreased to 0.4 ± 0.2 mM g^{-1} dw d^{-1} after 30 d. It was also shown in former studies that the flux of leached components of *Rhizophora mangle* leaves was high in the first hours of an incubation and decreased over time, even though fluxes calculated there were lower than in the current experiment (Fig. 6, Davis III et al. 2003, Maie et al. 2006).

Insert Fig. 6

4.1.2 Species

The DOC concentrations were significantly different between species, being highest for *Acanthus ilicifolius, Avicennia marina* and *Derris trifoliata*. *Rhizophora apiculata* showed intermediate values with 13 mM g^{-1} dw after 6 d, which were already higher than those of *Rhizophora mangle* in the Everglades with 4 ± 1 mM g^{-1} dw after 36 d and with 3 ± 1 mM g^{-1} dw after 21 d (Davis III et al. 2003, Maie et al. 2006).

A decrease in the DOC concentration is likely to be caused by the growth of bacteria and fungi which can consume DOC directly (Odum & Heald 1975, Cundell et al. 1979, Camilleri & Ribi 1986, Alongi et al. 1989). On *Avicennia* and *Rhizophora* trees 28 different marine fungal species were found, most of them saprophytes or pertophytes (Kohlmeyer 1969). The fungi *Phytophthora vesicula* and *Phytophthora spinosa* var. *lobata*, the most abundant colonizers of *Rhizophora mangle* leaves, can populate 75-100% of the leaves within the first 24 h of leaf submergence (Fell & Master 1975, 1980). In a former leaching study on *R. mangle* with poisoned and pure distilled water in the Florida Coastal Everglades it was shown that a part of the DOC leached from senescent plants can be consumed by microbes within three days after leaching (Maie et al. 2006).

The decomposition rate of mangrove litter may be high for *Sonneratia* (with high initial nitrogen concentrations) and low for *Rhizophora* (with higher levels of inhibitors such as tannins) (Ashton et al. 1999). A reason for the different species leaching rates could be the different leaf composition, e.g. in proteins, polyphenols and tannin concentrations (Steinke et al. 1990, Robertson et al. 1992, Wafar et al. 1997, Basak et al. 1998). Another reason for the high DOC concentration in the experiment with *A. marina* could be the defects of leaves due to insect grub areas. An increase of the total surface can result in higher rates of both microbial activity and leaching (Harrison & Mann 1975). It is conceivable that the observed differences in leaching speed between species analyzed in this experiment largely depend on the biochemical composition of the leaves.

4.1.3 Salinity

No significant differences were found in most of the species between the four salinity concentrations except for *Aegiceras corniculatum* and *Sonneratia caseolaris.* Nevertheless previous studies showed that the presence or absence of freshwater input into mangrove creeks seem to be an important factor affecting the direction and magnitude of material fluxes (Robertson et al. 1992). It was suggested that leaching may be slowed down by the presence of salt ions (Lush & Hynes 1973, Steinke et al. 1993). *R. mangle* decomposes faster in sea water then in freshwater systems in the North River of the Everglades, but it was proposed that this is rather due to the larger populations of grazing organisms present in the salt water (Odum & Heald 1975). It was also stated earlier that the osmotic pressure of Milli-Q water is different from natural and especially from saline water. Therefore, cells that can not tolerate a sudden change in osmotic pressure might burst in the beginning of an incubation with fresh water leading to an initially quicker release of DOM (Maie et al. 2006). In the current study the salinity had little or no effect on the leaching rates of DOC. The effect of salinity can not be generalized as the influence varies among species.

4.1.4 Location and leaf properties

Many factors can influence leaf leaching rates such as the duration of submergence (Webster & Benfield 1986, Robertson 1988, Mackey & Smail 1996), microbial activity or breakdown by invertebrates as well as physical parameters like waves and currents (Robertson 1986, Twilley et al. 1986, Davis III et al. 2003). The location where leaves fall on the floor, and therefore the distance to the water channels as well as the water residence time in a creek or lagoon has an impact on the amount of DOC leached into the water. When tree species are located in the higher intertidal and where they are surrounded by other trees with litter holding roots, leaves are less susceptible to export (Twilley et al. 1986, Schories et al. 2003).

4.2 Vegetation distribution affecting DOC fluxes in the Segara Anakan Lagoon

4.2.1 Western and central lagoon

In the western and central lagoon *Avicennia alba* is the dominant mangrove tree species, followed by *Aegiceras corniculatum* and *Sonneratia caseolaris,* but tree density especially of adult trees and the coverage by understorey species were low (Hinrichs et al. 2009). The DOC concentrations were more than one third higher for *A. corniculatum* than for *S. caseolaris* making the former species a quantitatively more important DOC source in the central part of the lagoon.

Area C and W are dominated by the shrub species *Acanthus ilicifolius* making up to 78% of the total vegetation, except for one site where *Derris trifoliata* is most abundant (60%) (White et al. 1989, Hinrichs et al. 2009). Uncontrolled deforestation and newly accreting mud banks fed mainly by the high sediment input from the Citanduy River probably promote the growth of these shrubs. Since both species prefer soft sediment (Hogarth 2007) and *D. trifoliata* thrives best at low salinity whereas *A. ilicifolius* is relatively insensitive to salinity gradients (Joshi & Ghose 2003, Ye et al. 2005) they are more abundant in the central and western lagoon where freshwater input is high (Hinrichs et al. 2009). The higher abundances of these species in the central area together in combination with the riverine input (e.g. agriculture, rice fields) of DOC may be responsible for the maximum DOC concentration of the entire lagoon measured in the Citanduy mouth (1.2 mM). The high abundances of *Acanthus, Avicennia* and *Derris* in combination with the highest leaching rates during the experiments suggest that leaf leaching is a quantitatively important source of DOC in the western and central parts of the SAL.

4.2.2 Eastern lagoon

Aegiceras corniculatum, Nypa fructicans and *Rhizophora apiculata* are the most abundant species in the eastern lagoon (Hinrichs et al. 2009). Therefore the highest possible contribution to the DOC pool in the eastern lagoon could come from *A. corniculatum* (27.4 mM g^{-1} dw) and *R. apiculata* (13.3 mM g^{-1} dw). *Avicennia marina* has higher abundances in the eastern part (up to >25% of the tree species composition) than in the central and western part of the lagoon (<10% of the tree species composition) (Hinrichs et al. 2009). Even though its total abundance is less then for the former two species, it can also provide high DOC concentrations to the lagoon with up to 52.9 mM g^{-1} dw. *Bruguiera gymnorrhiza* appears with <10% of the tree species composition in the eastern lagoon. Due to its low abundance and low leaching rates with 4.1 mM g^{-1} dw this species is not an important DOC source for the

SAL, whereas *A. corniculatum, A. marina* and *R. apiculata* could highly contribute to the DOC inventory.

4.2.3 Other contributions to the DOC inventory of the Segara Anakan Lagoon

Our study demonstrates only the potential input of DOC from leaf leaching into the lagoon. It was also shown that woody parts, pneumatophores and roots can also leach considerable amounts of DOC and nutrients (Albright 1976, Van der Valk & Attiwill 1984, Robertson & Daniel 1989a). Even though leaching rates of roots, twigs and bark were not examined in the current study, these parts possibly may also contribute to the DOC standing stock in the SAL.

4.3 Fate of mangrove DOC in the Segara Anakan Lagoon

DOC concentrations in the leachate were higher than the DOC concentration in the SAL, in some cases by orders of magnitude. According to Meyer et al. (1998) leaching from leaves contributed up to 37% to the DOC in a southern Appalachian stream, but other sources can also provide significant organic carbon inputs like allochthonous riverine or marine material, autochthonous production by benthic or epiphytic micro- or macroalgae, and local water column primary production by phytoplankton (Bouillon et al. 2004). Benthic flux experiments in the SAL have shown that there is no efflux of DOC from mangrove sediments. It is conceivable that microbes can consume most of the leached DOC from mangroves in the SAL, which might be one major reason for the low concentration in the lagoon.

The DOC leached out of leaves in the SAL can either be exported or consumed by the local biota. It has been suggested for the Florida Coastal Everglades that riparian tree species like the red mangrove (*Rhizophora mangle*), cattail and sawgrass are the main

DOC contributors to the water (Maie et al. 2006) or that DOM mainly derived from litter leachate in the mangrove-fringed Caeté Estuary (Dittmar & Lara 2001b). Due to outwelling >75% of the organic carbon can be lost within the first weeks of leaf fall (Robertson et al. 1992, Dittmar & Lara 2001b, Schories et al. 2003). A reason for the low DOC concentrations, especially in the eastern and western part of the lagoon (0.24 and 0.20 mM), could be the short residence time of the water. The flushing time is about one to three days in the eastern and western area and increases to about three to 18 days in the central part during the dry season (Holtermann et al. 2009). None of the species in the current study showed a leaching maximum within the first three days. Because of the longer residence time of water in the central lagoon one might expect a higher DOC concentration there. However, this was not observed in the current study, most likely due to leaf consumption by crabs. Nordhaus et al. (2009) found that the mean density of macrobenthos in the lagoon is 2.5-fold higher in the central than in the eastern part of the Segara Anakan. This indicates that in the central lagoon leaves might be consumed before leaching can be completed. Mangrove detritus is known to be an important food source for decomposer food webs such as macroinvertebrates like sesarmid crabs, fiddler crabs and gastropods (Bouillon et al. 2002, Kristensen & Alongi 2006). Crabs are capable of removing 30-90% of the litter fall (Robertson 1986, Robertson & Daniel 1989b, Schories et al. 2003, Kristensen et al. 2008). *Derris trifoliata* had very high DOC concentrations with a maximum after 14 d of incubation in the current study. Yellow leaves of this vine were mainly consumed by *Episesarma singaporense, E. versicolor* or *Perisesarma darwinense* in the SAL (Herbon, subm.). If this plant species is consumed within the first days after leaf fall this would highly reduce the possible DOC input into the lagoon.

4.4 Implications for ecology and carbon cycling

Between 1987-2006 major changes occurred in the SAL, i.e. a conversion of mangrove-covered area into agriculture and aquaculture (Ardli & Wolff 2009). If logging of mangrove trees and the reclamation of land, e.g. for agriculture, continues in the SAL this could lead to a reduction of litterfall due to a lower tree abundance. For example, it has been shown in an Appalachian stream, that a reduced litterfall into the water reduced the concentration in the stream, export, and instream generation of DOC. Simultaneously, the abundance of leaf-shredding invertebrates also decreased which was supposed to have a significant effect on other detritivorus benthic invertebrates and the whole food web (Meyer et al. 1998).

But not only a change in litterfall rates, but also a change in community composition might occur. Over the past 25 years the central area of the Segara Anakan Lagoon was dominated by *Rhizophora* and *Bruguiera* species (White et al. 1989), but nowadays they are less abundant. This changed due to deforestation or changing environmental conditions (Hinrichs et al. 2009). It is known that due to logging in mangrove forests the free space can mainly be invaded by species like *Acanthus* and *Derris* (Hogarth 2007). The settling of these shrub species can inhibit the growth of true mangrove species due to competition for light (Ashton & Macintosh 2002). It is conceivable that the increasing abundance of *Acanthus ilicifolius* in combination with its high leaching rates of DOC increases the DOC inventory of the lagoon.

In the current study we have shown a potential high DOC input from mangrove leaves into the SAL. Low DOC concentrations in the lagoon suggest that the DOC is rapidly consumed and/or exported. Litter processing varies with tree species and fauna like crabs. The DOC input of leaching is particularly important during the dry season when input from rivers like the Citanduy is low.

Acknowledgments

We thank Edy Yuwono and Husein Sastranegara for their support, Yuni Yumiarti for helping us in the field, Carolin Herbon, Anne Buhmann, Dana Pargmann and Alexandra Ostmann for their help and Matthias Birkicht for help with laboratory work. This study was supported by the Bremen International Graduate School for Marine Sciences (GLOMAR) that is funded by the German Research Foundation (DFG). Financial support by the German Federal Ministry of Education and Research (Grant No. 03F0471A) within the SPICE (Science for the Protection of Indonesian Coastal Marine Ecosystems) program is gratefully acknowledged.

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Figures

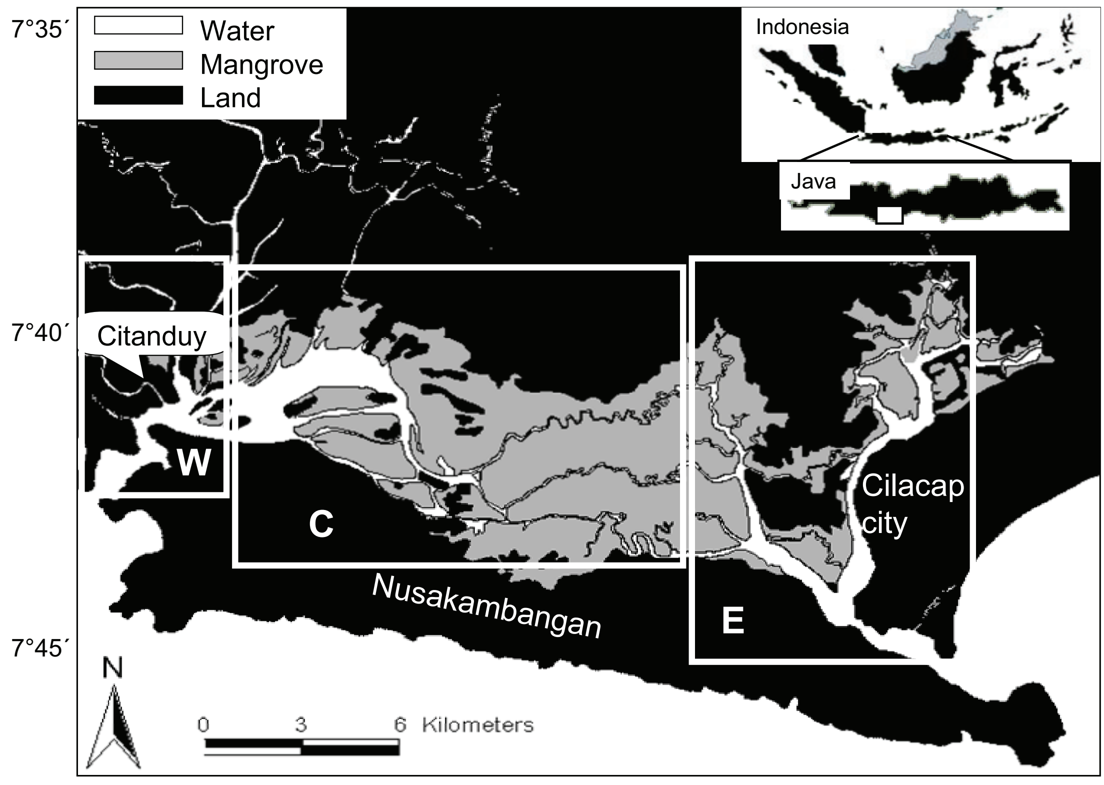
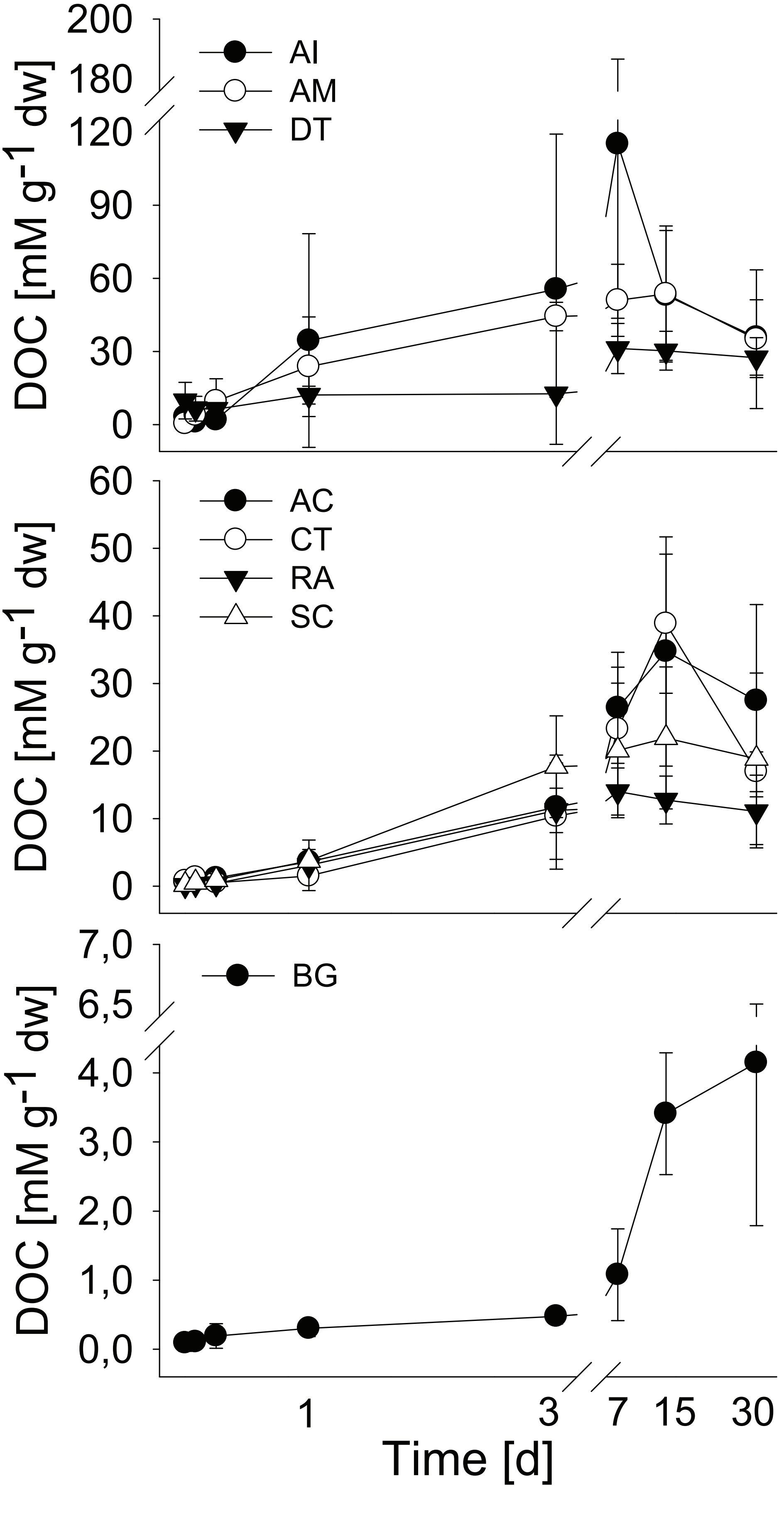
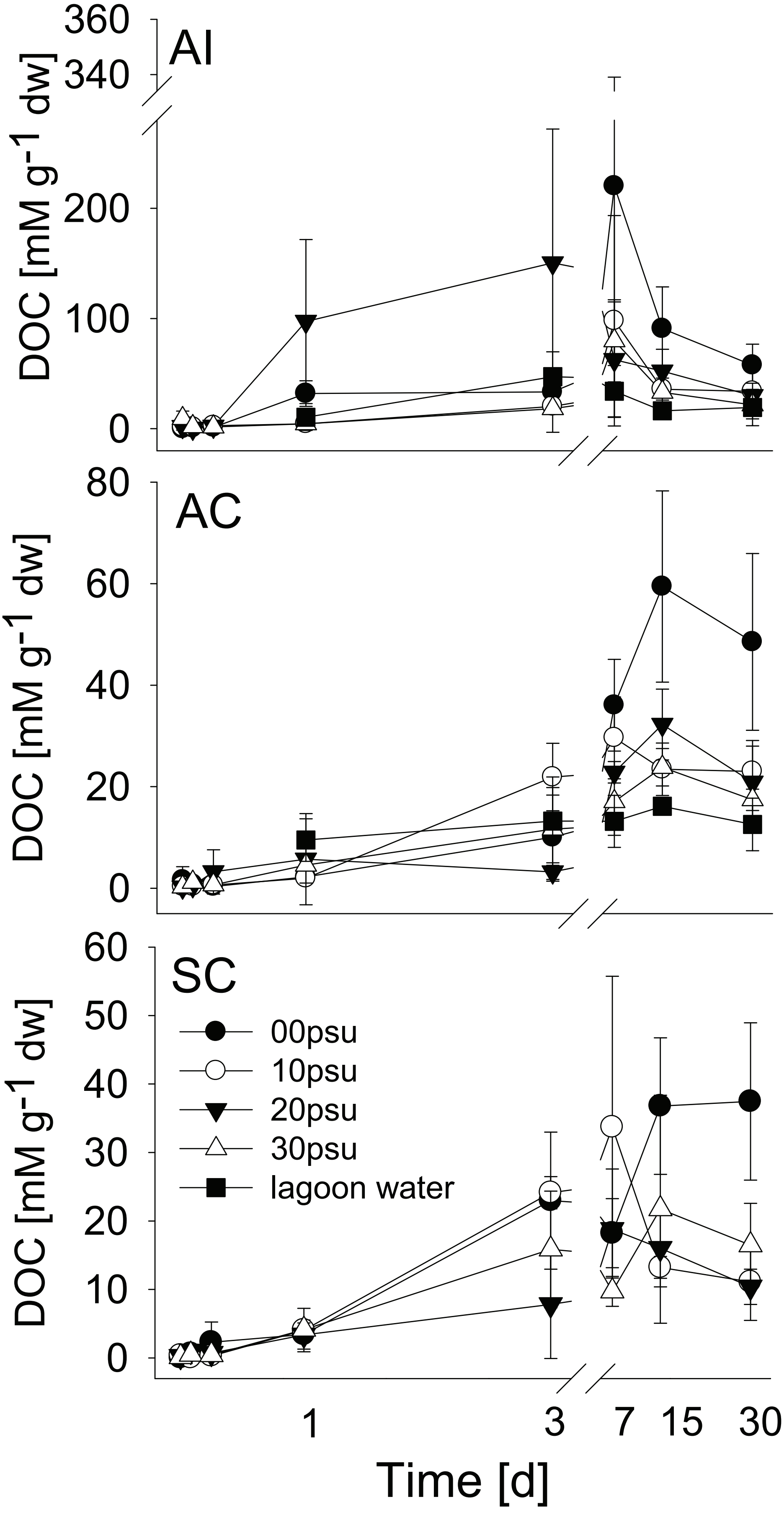


Fig. 1: Map of Segara Anakan including the Citanduy River and the three sampling areas (W= west, C= central, E= east).


AI
AM
DT
AC
CT
RA
SC
BG
DOC [mM g-1 dw]
Time [d]
200
180
120
90
60
30
0
60
50
40
30
20
10
0
7,0
6,5
4,0
3,0
2,0
1,0
0,0
1
3
7
15
30

649

Fig. 2: The concentration of dissolved organic carbon (DOC in mM g^{-1} dw ± S.D.) of the leaching samples (mean values for four salinity approaches), separated for clarity into the lowest concentration (lower graph), medium concentrations (middle graph) and the highest DOC concentrations (upper graph). (AC= *Aegiceras corniculatum*, AI= *Acanthus ilicifolius,* AM= *Avicennia marina*, BG= *Bruguiera gymnorrhiza*, CT= *Ceriops tagal*, DT= *Derris trifoliata*, RA= *Rhizophora apiculata*, SC= *Sonneratia caseolaris*).



AI
AC
SC
DOC [mM g-1 dw]
00psu
10psu
20psu
30psu
lagoon water
Time [d]
1
3
7
15
30

657

Fig. 3: The concentration of dissolved organic carbon (DOC in mM g^{-1} dw ± S.D.) of the leaching samples for *Aegiceras corniculatum* (AC), *Acanthus ilicifolius* (AI) and *Sonneratia caseolaris* (SC) over a time period of 720 h and four salinities (black circles: 0 g l^{-1}, white circles: 10 g l^{-1}, black triangles: 20 g l^{-1}, white triangles: 30 g l^{-1}) and lagoon water with 22.1 psu (black squares [AC and AI only]).

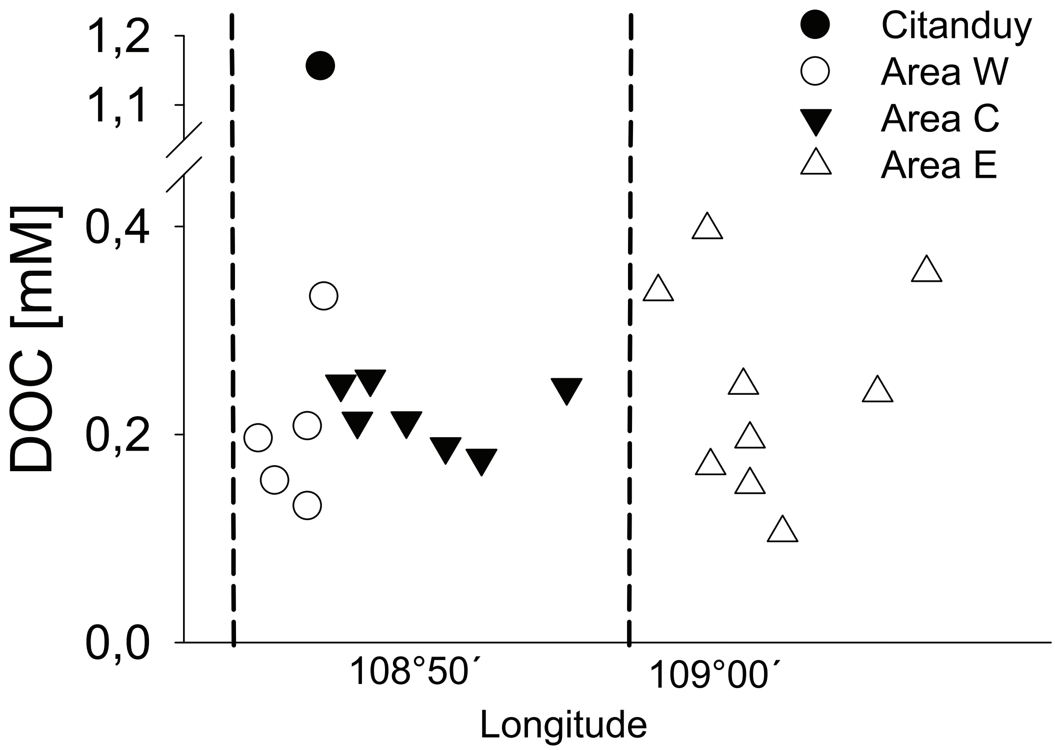


Fig. 4: The surface water concentration of dissolved organic carbon (DOC [mM]) in the three areas of the Segara Anakan lagoon. Dashed lines indicate the outlets to the Indian Ocean (right: western outlet, left: eastern outlet).

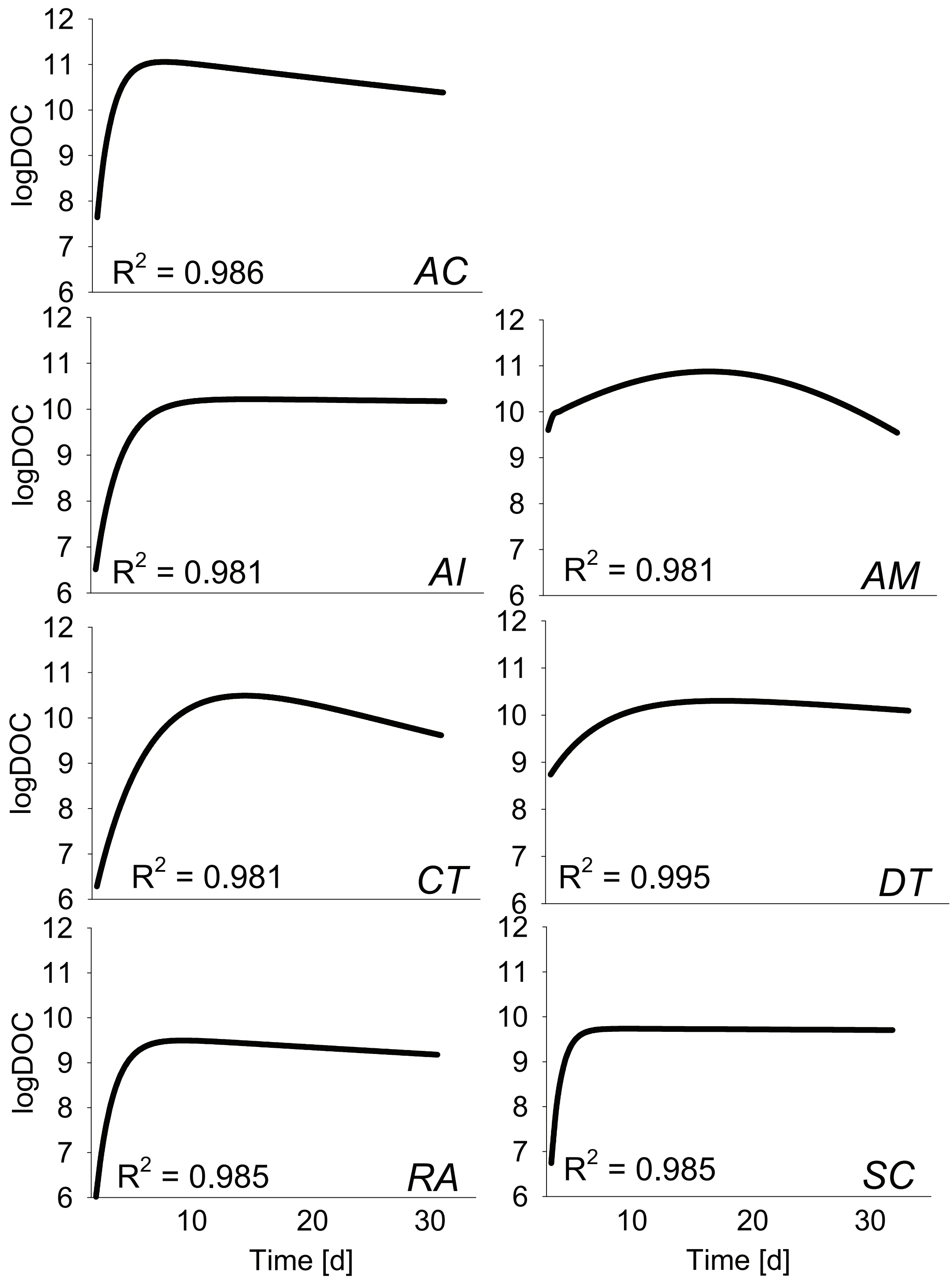


Fig. 5: The logarithm of DOC concentrations calculated by the non-linear regression over time (AC= *Aegiceras corniculatum*, AI= *Acanthus ilicifolius*, AM= *Avicennia marina*, CT= *Ceriops tagal*, DT= *Derris trifoliata*, RA= *Rhizophora apiculata*, SC= *Sonneratia caseolaris*).

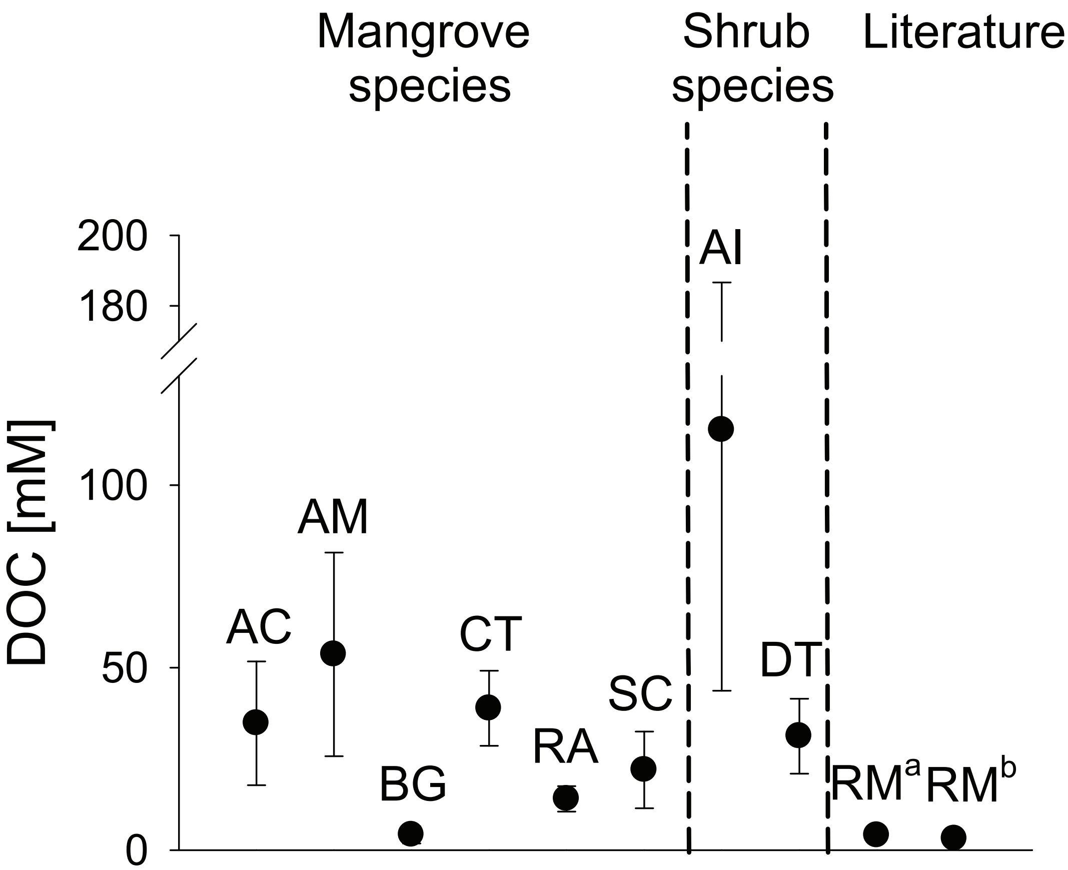


Fig. 6: Highest DOC concentrations (mM ± S.D. from four salinities) during the leaching experiment (AC= *Aegiceras corniculatum*, AI= *Acanthus ilicifolius*, AM= *Avicennia marina*, BG= *Bruguiera gymnorrhiza*, CT= *Ceriops tagal*, DT= *Derris trifoliata*, RA= *Rhizophora apiculata*, RM= *Rhizophora mangle* [[a]= Davies et al. 2003, [b]= Maie et al. 2006], SC= *Sonneratia caseolaris*).

Tables

Tab. 1: The interactions between species, time and salinity based on a three-way ANOVA. Significant p-values are labeled with a star (SS= sum of squares, Dgr. F= degree of freedom, MS= Means, F= test statistic of the F-test after Fisher, p= significance level).

	SS	Dgr. F	MS	F	p
Species	793.59	7	113.37	122.6	0.000*
Salinity	2.23	3	0.74	0.8	0.519
Time	1851.29	7	264.47	285.9	0.001*
Species*Time	265.16	21	5.41	1.5	0.112
Species*Salinity	28.79	49	1.37	5.9	0.000*
Salinity*Time	46.12	21	2.20	2.4	0.006*
Species*Time*Salinity	212.11	147	1.44	1.6	0.002*

Tab. 2: Parameters used for the non linear regression estimated by iterative fitting using the Marquard-Levenberg method (a= measure of the total DOC increase; b= coefficient for the speed of increase; c= measure for the total decrease; d= coefficient for the speed of decrease,; e= curvature term. Significances are marked with *), the time of the maximum concentration and the DOC concentration at the calculated maximum. (AC= *Aegiceras corniculatum*, AI= *Acanthus ilicifolius*, AM= *Avicennia marina*, CT= *Ceriops tagal*, DT= *Derris trifoliata*, RA= *Rhizophora apiculata*, SC= *Sonneratia caseolaris*).

	AC	AI	AM	CT	DT	RA	SC
a	6,36 *	5,67 *	5,53 *	5,81 *	8,56 *	4,86 *	4,81 *
b	0	0	0,00 *	0	0	0	0
c	5,04 *	4,60 *	4,30 *	6,57 *	2,13 *	4,79 *	4,94 *
d	-0,03 *	-0,02 *	-0,27 *	-0,01 *	-0,01	-0,03 *	-0,05 *
e			-0,15 e^{-5} *				
Calculated Maximum [h] / [d]	146 / 6	322 / 13	336 / 14	255 / 11	343 / 14	188 / 8	167 / 7
Calculated DOC at max [mM]	27.39	63.33	52.87	33.71	29.82	13.30	16.88

Tab. 3: Changes in the weight loss (%) of leaves, roots and wood, carbon loss (%) of leaves, DOC concentration and fluxes during leaf decomposition (AC= *Aegiceras corniculatum*, AI= *Acanthus ilicifolius*, AM= *Avicennia marina*, AG= *Avicennia germinans*, AO= *Avicennia officinalis*, BG= *Bruguiera gymnorrhiza*, CT= *Ceriops tagal*, DT= *Derris trifoliata*, RA= *Rhizophora apiculata*, RM= *Rhizophora mucronata*, RS= *Rhizophora* stylosa, SA= *Sonneratia alba*, SC= *Sonneratia caseolaris*). Changes of weight loss in the current study are means of the four salinities and the three replicates.

Species	Time [days]	Weight loss [%] leaves	Weight loss [%] roots (r) /wood (w)	Carbon loss [%] leaves	DOC concentration [mM g^{-1} dw]	DOC Flux [mM g^{-1} dw d^{-1}]	Technique	Country	Reference
AC	1	5 ± 6			3.6 ± 1.8	3.6 ± 1.8	Incubation	Indonesia	current study
	30	24 ± 10			27.5 ± 1.4	0.9 ± 0.5			
AI	1	25 ± 17			34.5 ± 43.8	34.5 ± 43.8			
	30	65 ± 16			35.7 ± 15.5	1.2 ± 0.5			
AM	1	14 ± 16			23.8 ± 20.4	23.8 ± 20.4			
	30	36 ± 24			35.0 ± 28.4	1.2 ± 0.9			
BG	1	13 ± 19			0.3 ± 0.1	0.3 ± 0.1			
	30	32 ± 26			4.2 ± 2.4	0.1 ± 0.08			
CT	1	5 ± 9			1.5 ± 0.6	1.5 ± 0.6			
	30	16 ± 23			16.9 ± 2.9	0.7 ± 0.1			
DT	1	6 ± 14			12.1 ± 3.6	12.1 ± 3.6			
	30	29 ± 20			27.5 ± 8.2	0.9 ± 0.3			
RA	1	4 ± 4			30.9 ± 3.7	30.9 ± 3.7			
	30	11 ± 12			11.1 ± 5.4	0.4 ± 0.2			
SC	1	7 ± 15			3.7 ± 0.4	3.7 ± 0.4			
	30	40 ± 35			18.9 ± 12.7	0.6 ± 0.4			
AM	28	30	12 (r)				Tube incubation	New Zealand	(Albright 1976)
RM	9	14-40					Incubation	USA (Florida)	(Camilleri & Ribi 1986)
	154	95	52 (r)						
RM	2				0.8 ± 0.4	0.4	Incubation	USA	(Maie et al. 2006)

								(Florida)	
	36				4.0 ± 0.9	0.1 ± 0.01			
RM	6	18					Incubation	Bahamas	(Benner et al. 1988)
RM	1	8			0.8 ± 0.3	1.3 ± 0.6	Leaching and litterbag	USA (Everglades)	(Davis III et al. 2003)
	21	49		51	3.1 ± 0.9	0.3 ± 0.1			
AM	3-9	13-40	10-15 (r)				Litterbag	Australia	(Van der Valk & Attiwill 1984)
	230-270	80-90	60 (r)						
AM	30	~30-35	~0-8 (w)				Litterbag	Australia	(Mackey & Smail 1996)
	150	~58-95	~5-50 (w)						
RS	156	40,3		~40			Litterbag	Australia	(Robertson 1988)
AM	156	61,5		~60					
CT	156	45,5		~50					
RA	15	~70		~75			Litterbag	India	(Wafar et al. 1997)
	90	100		~97					
RM	15	~60		~65					
	105	100		100					
SA	15	~60		~70					
	105	100		100					
AO	15	~70		~70					
	90	100		100					
RM	70			17			Litterbag	USA (Florida)	(Cundell et al. 1979)
RM	25	15		10			Incubation	USA	(Rice & Tenore 1981)
	150	20		13					
AG	25	15		33					
	150	35		33					

Nutrient dynamics in the mangrove-fringed Segara Anakan Lagoon, Java, Indonesia

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Abstract

The Segara Anakan Lagoon is highly affected by human activities such as mangrove logging, mangrove conversion into rice fields and sedimentation. Spatial and temporal variations in the inventory of dissolved inorganic nitrogen (DIN), dissolved organic nitrogen (DON), phosphate and silicate were investigated in this lagoon with regard to seasonality over a period of five years, tidal variations and benthic recycling. The lagoon exchanges water with the Indian Ocean through a western and an eastern outlet. The nutrient inventory is mainly governed by the high inputs from the Citanduy River in the west and therefore by the agriculture-dominated hinterland. Oceanic water only influences the western lagoon during high spring tide whereas the eastern outlet mainly receives water from the Indian Ocean through Penyu Bay. The Serayu River discharges into this adjacent bay and therefore indirectly influences the hydrology of the eastern lagoon. Benthic recycling is not a major source of nitrogen, phosphate and silicate during the dry season when the river discharge is low. Nutrient concentrations were low to moderate (DIN 0.7 – 29.7 µM, PO_4^{3-} <1.1 µM) which might be due to the short residence time of the water in the lagoon as well as due to uptake by bacteria, phytoplankton, and phytobenthos.

Keywords: dissolved inorganic nutrients, nitrogen, benthic recycling, tidal cycle, mangrove, Segara Anakan Lagoon

1. Introduction

Mangroves are known to play an important role due to their high productivity with 20-50 t C ha^{-1} y^{-1} and their influence on the carbon and nutrient budget of the coastal zone (1992, Alongi et al. 1998, Clough 1998, Jennerjahn & Ittekkot 2002). Mangroves occur in the intertidal and act as a nutrient filter between land and sea (Clough et al. 1983, Robertson & Phillips 1995, Rivera-Monroy et al. 2004) which can prevent coastal ecosystems like seagrasses and coral reefs from eutrophication. But these ecosystems are affected by anthropogenic impacts (Ardli and Wolff, 2009; Moffat, 1998) and decline at a rate of 2% per year (Valiela et al., 2001). Various factors can influence the direction and magnitude of material flux, such as freshwater input, tidal range, geomorphology, soil chemistry, oxygen availability, mangrove plant biomass and community structure (Boto & Wellington 1988, Alongi et al. 1992, Robertson et al. 1992, Ayukai et al. 1998). The amount of water is important as water availability controls plant nutrient uptake, microbial transformation in sediments and reactant transport (Baldwin and Mitchell, 2000; Belnap et al., 2005; Bouillon et al., 2007; Chen et al., 2007; Duarte and Cebrián, 1996; Mulholland, 1992; Welter et al., 2005). Due to anthropogenic inputs nutrient concentrations increased steadily in recent decades in various ecosystems (Moffat, 1998; Nedwell, 1999; Rabalais et al., 1996; Scheren et al., 2004; Seitzinger et al., 2005; 2010; Smith et al., 2003). Nutrients originate from agricultural sources, industrial and urban sewage and atmospheric deposition as well as from natural sources like fixation of atmospheric nitrogen by cyanobacteria and release by microbial decomposition of organic material (Hogarth, 2007; Howarth et al., 1996). The exchange of dissolved inorganic nutrients between intertidal areas and the water column can either occur through diffusive fluxes across the sediment-water interface during inundation or through the seepage of porewater into the water column during low tide (Ovalle et al. 1990, Bava & Seralathan 1999, Lara & Dittmar 1999, Bouillon et al. 2007c, Chen et al. 2007). Sediments are thought to play a major role in the transformation of biologically active elements due to benthic nutrient regeneration at the sediment-water interface (Devol, 1987; Kristensen, 1988; Lock and Hynes, 1976; Nedwell, 1999; Sloth et al., 1995). This supply can support a substantial part of primary production (Friedrich et al. 2002, Jennerjahn & Ittekkot 2002). Benthic nitrogen regeneration supplies 26-101% of the phytoplankton demand in coastal zones (Kristensen, 1988).

It has been shown that high DIN and phosphate fluxes are correlated with high population densities and high runoff in humid areas (Smith et al., 2003). The nutrient inventory of the Segara Anakan Lagoon (SAL) is controlled by a mixture of both anthropogenic and natural sources and processes. It was stated earlier that the lagoon is oligotrophic to eutrophic but the system is highly variable and no clear trend was identified (Jennerjahn et al., 2008). Therefore we investigated the nutrient inventory in the SAL over a period of five years with regard to seasonality as well as tidal variations and benthic recycling. The following questions were raised: a) What are the sources and sinks in the SAL during the dry and the rainy season? b) What influences the dispersal of nutrients in this lagoon? c) Is benthic recycling a major source of nutrients during the dry season when river discharge is low?

2. Material and Methods

2.1 Study area

The SAL, which is located in south central Java (108°46′E – 109°03′E, 7°35′S – 7°48′S), is a mangrove fringed lagoon separated from the Indian Ocean by the rocky mountainous island of Nusakambangan (Fig. 1). The lagoon has two connections with the Indian Ocean. The mangrove forest is considered to be the largest remaining single mangrove stand in the south coast of Java with >9000 ha in 2006. But anthropogenic impacts like urbanization, cultivation for agriculture (mainly rice fields) and aquaculture cause habitat destruction. >50% of mangrove area were converted into different land use types within the last 30 years (Ardli and Wolff, 2009). The lagoon became already in the 19th century narrower and shallower due to an increasing sediment input mainly from the Citanduy River in the western part. The distribution of sediment is governed by water circulation patterns, which are mainly driven by tide and freshwater discharge. Freshwater input into the lagoon increases considerably during the rainy season, particularly due to the Citanduy (Purba 1991, Yuwono et al. 2007a, Yuwono et al. 2007b).

Insert Fig.1

The tropical humid climate is governed by the monsoon and therefore divided into a rainy season (November till March, annual precipitation: 3000-3500 mm) and a dry season (April till October) (White et al., 1989; Whitten et al., 2000). Water quality and biogeochemistry display temporal and spatial variability, e.g. in physical factors like salinity and turbidity (Purba, 1991; Yuwono et al., 2007). The semidiurnal tide ranges between 0.4 m during neap tide and 1.9 m during spring tide (White et al., 1989). The Citanduy is the fifth largest river of Java in terms of discharge with 227 $m^3 s^{-1}$ (dry season 171 $m^3 s^{-1}$, rainy season 283 $m^3 s^{-1}$) (Whitten et al., 2000). It had a catchment area of 3,520 km^2 in 1991 which is approximately 80% of the overall Segara Anakan catchment area (Purba, 1991). The eastern water body with the Donan catchment area has a freshwater input two orders of magnitude less than the Citanduy (Holtermann et al., 2009). A total freshwater inflow volume was estimated to be at least 5 x 10^9 m^3 whereas the seawater input through the western outlet is about 29 x 10^6 m^3 for spring tide and 10 x 10^6 m^3 for neap tide (Purba, 1991). The central lagoon is affected by tidal water movement and by the discharge of the Citanduy, Cibereum and Cikonde River (Purba, 1991; Yuwono et al., 2007).

2.2 Sampling

Sampling campaigns in the SAL were performed in May and September 2004, February and September 2005, January and August 2006 (for these expeditions only nutrient data are available) as well as in September 2007, February and September 2008 and February and September 2009. Water samples were taken at 23 stations in the lagoon (one in the Citanduy River, six in the western area, seven in the central area and nine in the eastern area).

2.2.1 Water sampling

The conductivity [mS cm^{-1}] was measured in situ. 50 ml of surface water for inorganic nutrient (ammonium, nitrate, nitrite, phosphate and silicate) analysis were filtered through syringe filters (pore size 0.45 µm) into PE wide neck bottles, preserved with a 4% mercury chloride solution and stored dark and cool until analysis. 500 ml of surface water was stored cool and dark in a PE canister. This water was filtered through Whatman GF/F filters for chlorophyll measurements.

2.2.2 Sampling during tidal cycles

For tidal cycle measurements diel sampling campaigns were performed during spring and neap tides between October 2008 and January 2009 under La Niña conditions (NOAA, 2008). Tidal cycle periods were estimated by using the WXTide 32 software in the city of Cilacap. In addition, a computer simulation of the hydrodynamics of Segara Anakan was used (Holtermann, pers. comm.). Water samples were taken at five stations in the lagoon: the Citanduy River (station A), the western outlet (station B), the central lagoon (station C), the eastern outlet (station D) and the Sapuregel River (station E). Water samples were collected hourly over 12 hours and every second hour for the following 12 hours. Water samples were taken for inorganic nutrient measurements. At the same time the conductivity was measured.

2.2.3 Flux estimation

Nutrient flux estimations were approximated by multiplying water discharge (Q) and material concentration (c) at time t. Hence, the net flux was calculated by adding up the flux increment over a full tidal cycle (24 h):

$$F = \sum_{t=0}^{24} (ct * Qt)$$

This formula was simplified from the *Eulerian* approach (Boto & Wellington 1988, Alongi 1996, Alongi et al. 1998, Ayukai et al. 1998, Dittmar & Lara 2001b).

2.2.4 Incubation experiments

Core incubation experiments were conducted at four stations in the SAL during September and October 2009. Three cores were taken per station during high tide 15 m from the low-shore line. Two plexiglass cores (length: 40 cm, diameter: 7 cm) were pressed ~20 cm deep into the sediment, taken out and sealed with a cap. The core was filled with lagoon water and closed with a lid on the upper end without air bubbles in the system. The lid was prepared with two plastic tubes of which one was attached to a syringe for sampling and the other one with a plastic bag which contained lagoon water. For core incubations sediment free of pneumatophores was used. To test the effect of phytobenthos one of these cores was wrapped in dark tape. A third core contained lagoon water only. Samples were taken during the first six hours every hour, during the following six hours every second hour and a final sample was taken after 24 hours. Due to problems with the electrical pumps the water in the cores was mixed manually by a gentle drawing up the syringe and pressing the water into the core again before sampling. During this procedure the attached water bag was sealed with a one-way-plug and opened again for sampling. At each sampling time 20 ml of water were taken from the core with the syringe to measure the oxygen content with an oxygen electrode (data available only for station 3 and 4). This water was filtered afterwards through a Minisart syringe filter (pore size 0.45 µm) and taken for inorganic nutrient analysis. The concentrations measured were corrected for the replacement of the sampled volume by lagoon water.

2.2.5 Sample analysis

The conductivity [mS cm^{-1}] was measured with a WTW MultiLine 340i multiparameter instrument. The salinity was calculated with conductivity and temperature.

Samples for the analysis of total dissolved nitrogen (TDN) were combusted in a Teledyne Tekmar Apollo 9000 Combustion analyzer at 800°C. Inorganic nutrient samples were measured in an elemental autoanalyzer SKALAR-SANplus system and detected spectrophotometrically as a coloured complex (Grasshoff and Koroleff, 1996). Ammonium was below the detection limit. Therefore dissolved inorganic nitrogen (DIN) consists in the following of nitrate and nitrite (determination limits: nitrate: 0.04 µM, nitrite: 0.05 µM, ammonium: 0.06 µM, phosphate: 0.06 µM and silicate: 0.19 µM; coefficient of determination: <3.4%).

For the chlorophyll a measurements the GF/F filters were cut and the suspended matter on the filter was dissolved in 9 ml acetone (90%). The solution was stored cold and dark for 24 hours, centrifuged and measured with a Turner 10-AU fluorometer.

2.3 Calculations and statistical analysis

The DON concentration was calculated by subtracting the dissolved inorganic nitrogen from the total nitrogen. The total oxygen uptake (TOU) (mmol m^{-2} h^{-1}) during the incubation experiment was calculated by using the formula:

$$TOU = \partial c * h * 24/((\partial t/60) * 100)$$

where δc = change in concentration, δt = change in time and h= height of water column. Fluxes were calculated by the following equation, modified after Bartoli et al. (2003):

$$Fx = \frac{(Cf - Ci) * V}{A * t}$$

F_x = flux of the x species [µM m^{-2} d^{-1}]

C_f = final concentration of x [µM]

C_i = initial concentration of x [µM]

V = volume of water [l]

A = surface area [m^2]

t = incubation time [d]

Fluxes for the core which contained lagoon water only were calculated using the same formula but without parameter A.

Differences between years, seasons and areas were tested with a three-way ANOVA using STATISTICA 9. Due to high variations in the data set the p-values were calculated by a simulation after Westfall and Young (1993). Test decisions base on a critical significance level (p-value) of 5%.

3. Results

3.1 Lagoon water concentrations

Chlorophyll a values were low during both the dry and the rainy season 2008 and 2009 with an average concentration of 4.0 µg l^{-1} (range: 1.5 – 6.8) during the rainy and 0.1 µg l^{-1} (range: 0.1 – 0.2) during the dry season.

Silicate concentrations were significantly higher during the rainy season (RS) than during the dry season (DS) and showed a west-east gradient (Fig. 2, Tab. 1). Highest concentrations were measured in the Citanduy River (RS: 226.5 ± 67.7 µM; DS: 38.5 ± 30.4 µM) and lowest in the eastern lagoon (RS: 78.0 ± 40.9 µM). During the dry season no significant differences were observed between the eastern, central and western lagoon. Higher silicate concentrations were observed in the western and central areas.

Insert Fig. 2 and Tab. 1

Nitrate and nitrite concentrations were significantly lower during the dry season. A west-east gradient was observed for nitrate during both seasons with highest concentrations in the Citanduy River (RS: 29.7 ± 4.5 µM, DS: 8.3 ± 10.4 µM) and lowest in the eastern area (RS: 2.9 ± 1.2 µM, DS: 0.7 ± 0.4 µM). Nitrite concentrations showed no clear spatial trend but were also significantly higher during the rainy season with a maximum in the eastern area (24.6 ± 31.3 µM). During the dry season the concentration did not differ between areas with an average of 1.6 ± 0.2 µM. No trend over the years was observed both for the dry and the rainy seasons.

Phosphate concentrations were lower during the dry season and no significant spatial gradient was observed. Mean concentrations in the Citanduy and the three areas ranged between 0.2 and 1.1 µM with a maximum of 2.6 µM during the rainy season 2004.

The N:P ratios had average values of 32.6 during the rainy and of 12.6 during the dry season (Fig. 3). The ratio was always higher in the western area and in the Citanduy River and lower in the eastern area. As no phosphate data were available for January 2005 the N:P ratio was not calculated. No temporal trend was observed during the dry season. Nevertheless the N:P ratio was much higher during the last two sampling times during the dry the season.

Insert Fig.3

The organic nitrogen concentration was higher during the dry season (September 2008 and 2009) than during the rainy season (February 2009) except for the eastern lagoon, where the DON was slightly but not significantly higher than the DIN (Fig. 4). The organic nitrogen concentration ranged between 10.3 and 37.8 µM during the dry season and between 3.2 and 13.1 µM during the rainy season.

Insert Fig.4

3.2 Tidal cycles

The highest concentration of phosphate was found at station B in the western outlet (5.1 µM) and lowest at station D in the eastern outlet (<0.1 µM) but no clear pattern in relation to salinity was observed (Fig. 5). DIN consisted mainly of nitrate as nitrite concentrations were close to the detection limit. Silicate and DIN concentrations showed clear diel patterns. High silicate fluctuations were found in the Citanduy River ranging from 12.1 to 235.8 µM during spring tide. In contrast, silicate fluctuated less during neap tide (193.2 to 238.5 µM). At station D, silicate concentrations varied less during spring tide (12.8 to 23.1 µM). However, a very high concentration of silicate (up to 118.5 µM) was observed at high neap tide. DIN variation displayed the same pattern as silicate. At station A the DIN concentration ranged between 0.1 to 33.1 µM and 23.1 to 33.9 µM during spring tide and neap tide, respectively. DIN concentration at the eastern outlet varied less during spring tide (0 to 1.3 µM) and increased to 7.2 µM at high tide during neap tide.

Insert Fig.5

Even in the Citanduy River nutrient concentrations showed daily fluctuations despite freshwater conditions. Silicate concentration ranged from 240.9 to 293.6 µM and DIN from 28.6 to 46.0 µM during neap tide.

In the Sapuregel (station E) which exchanges water with mangrove creeks, silicate and DIN displayed negative correlations with salinity fluctuation at spring tide ($\rho_{Si\text{-}salinity}$= -0.99; $\rho_{DIN\text{-}salinity}$= -0.87). Concentrations ranged from 20.3 to 106.6 µM for silicate and from <0.1 to 6.3 µM for DIN, respectively. Lowest concentrations were found during the early stage of low tide while the highest concentration levels were observed during slack low tide.

A water discharge of 2.5 x 10^6 m^3 d^{-1} was calculated through the western outlet both during neap and spring tide, whereas less water was discharged through the eastern outlet (0.7 x 10^6 m^3 d^{-1} at spring tide and 0.2 x 10^6 m^3 d^{-1} at neap tide). The input of the Citanduy River to the lagoon was between 7.8 x 10^6 m^3 d^{-1} (spring tide) and 5.8 x 10^6 m^3 d^{-1} (neap tide).

Silicate and DIN inputs from the Citanduy to the lagoon were always higher than the exports to the Indian Ocean through the western outlet (Tab. 2). In contrast, phosphate input from the River was lower than the export.

Insert Tab.2

3.3 Benthic recycling

The oxygen concentration decreased at both stations over time even though at station 4 an increase was observed within the first four hours. The TOU was higher at station 4 with 25 to 28 mmol m^{-2} d^{-1} than at station 3 with three to 19 mmol m^{-2} d^{-1}.

Silicate fluxes at station 2 and 4 in the three cores were down to -140.5 µM m^{-2} d^{-1} and between 1.3 to 2.7 µM m^{-2} d^{-1} at station 1 (Fig. 6). Due to high variations in the silicate concentrations fluxes could not be calculated for station 3. Phosphate were between -0.03 and -0.54 µM m^{-2} d^{-1} at station 4.

Insert Fig.6

The four sites differed in nitrogen concentration. Nitrite was <1 µM at all stations. A decrease in the nitrate concentration was observed at all four sites except for the dark and lagoon water core at station 3. Nitrate concentrations in the water column decreased with down to -14.4 µM m^{-2} d^{-1} at station 4 in the core with lagoon water. Only at station 2 in the lagoon water core the fluxes increased to 0.01 µM m^{-2} d^{-1}.

4. Discussion

4.1 Sources and dispersal of nutrients

4.1.1 Rivers and the Indian Ocean

Seasonal and spatial gradients were observed for nitrate and silicate concentrations as well as for the N:P ratio over a period of five years. Spatio-temporal variations of nutrient concentrations in the SAL can be explained by varying factors like hydrology, vegetation, land use and urbanisation (Jennerjahn et al., 2009). The Citanduy River is the major source of nutrients in the western and central part of the lagoon. The seasonal changes in the nutrient concentrations displayed that during the rainy season more allochthonous material from the hinterland is discharged through the SAL. It was assumed earlier that this nitrogen mainly originates from fertilizers (Jennerjahn et al., 2009). The gradient in the N:P ratio from the western to the eastern lagoon is probably related to the higher input of agriculture effluents in the western area. However, it has to be considered that only little nitrogen amounts can be taken up by plants at a very high N:P ratio. Also the silicate concentrations increased due to a strong weathering of soils at high rainfall. However, the nutrient concentrations were in the same range with other mangrove-fringed lagoons and estuaries like in Brazil, Mexico and Taiwan (Tab. 3). The strong nutrient concentration gradient from the western to the eastern lagoon is mostly related to agriculture effluents discharged by the Citanduy River whereas silicate originates from natural weathering of rocks and soils.

Insert Tab. 3

Nutrient concentrations in the Citanduy River were higher than in the central and eastern lagoon in the current study due to no dilution effect of seawater as shown by the constant freshwater conditions. Holtermann et al. (2009) calculated a Citanduy discharge of 350 m^3 s^{-1} during the rainy season. There, it was concluded that a high nutrient-rich Citanduy discharge (esp. during the rainy season) is enough to block the seawater intrusion into the lagoon during neap tide and to flush the entire lagoon. The nutrient inventory in the central lagoon is influenced both by the Indian Ocean and the Citanduy River but this impact varies with tidal conditions. It has been observed earlier in the SAL that nutrient concentrations in the central lagoon can be half of that in the Citanduy during the dry season (Yuwono et al., 2007). Higher nitrate values during low tide might be due to nitrification of ammonium which derives from porewater or due to porewater seepage of nitrate (Dittmar and Lara, 2001; Ovalle et al., 1990). We conclude that a tidal amplitude of 0.4 m during neap tide (White et al., 1989) is not enough to cause high fluctuations in nutrient concentrations in the Citanduy as well as at the western outlet (station B). There, oceanic water enters the lagoon only during the flood of spring tide. A stronger discharge of the Citanduy leads to less nutrient variations at the western outlet during a tidal cycle. Nevertheless it has to be considered that the data presented here are taken from the water surface but stratification can occur in this area at high tide (Holtermann pers. comm.). It is likely that saline water enters the lagoon in a subsurface flow above the sediment surface while the Citanduy discharge is exported at the surface.

At station D only little variation in salinity ~30 was observed. There, nutrient-poor seawater nourishes the lagoon. Interestingly, silicate and DIN concentrations increased during high tide when salinity dropped to 20.4. The Serayu River, which is besides the Citanduy the largest river on Java discharging directly into the Indian Ocean, flushes into Penyu Bay adjacent to the eastern outlet. Coastal circulation in this bay may lead to an input of the water from the Serayu River during high tide causing an increase in nutrient concentrations and a decrease in salinity. In the eastern lagoon where no river flows into the system, freshwater enters the lagoon only during the rainy season via surface runoff. Therefore, it is likely that the freshwater of the Serayu River was transported to the lagoon by tidal exchange via Penyu Bay.

4.1.2 Benthic recycling

Nutrient fluxes were low and differed between stations. Silicate fluxes were positive at station 1 and negative at station 2 and 4. However, it is known that sediments are usually a source of silicate to the water (Nedwell, 1999). Much higher fluxes than in the current study were reported for other tropical as well as temperate areas with between -77472 and 46728 µM m^{-2} d^{-1} (Fig. 4, Alongi, 1996; Friedrich et al., 2002; Spears et al., 2008). In these studies, the different nutrient fluxes were related to differences in both the quality and quantity of organic matter, the abundance and patchiness of phytobenthos, temperature as well as in the sediment structure, e.g. grain size.

No phosphate flux was observed in our SAL cores indicating that the uptake of phosphate was almost in equilibrium with the phosphorus release. However, in the tropical Caeté Estuary or the temperate Danube River where phosphate input is also low, the benthic recycling of this nutrient is an important factor in sustaining a high productivity (Friedrich et al., 2002; Ovalle et al., 1999). In the latter study the near-shore recycling of phosphate and silicate accounted for 50% and 35% of the river input, respectively. There, it was suggested that low DIP concentrations can be due to the formation of insoluble iron-manganese phosphate complexes and/or the adsorption to the sediment (Boynton and Kemp, 1985 and references therein; Clough et al., 1983; Schwendenmann et al., 2006). Nitrate fluxes were different between the three cores at station 2 with highest fluxes into the sediment in the light core but also at station 4 with highest nitrate uptake in the lagoon water core. However, it has been shown that sediments can act as a very efficient sink for nitrogen due to burial of detrital organic nitrogen and denitrification which reduces nitrate both at the oxic sediment layer and from the water column (Billen et al., 1989; Eyre and Ferguson, 2005) as well as incorporation into microbial tissues like fungal melanins (He et al., 1988). As the fluxes were low and mostly directed into the sediment it appears that benthic recycling is not a major source of nutrients in the SAL during the dry season.

Insert Tab.4

4.1.3 Mangrove leaf leaching

The DON concentration showed higher concentrations during the dry season compared to the rainy season in 2008/2009. It has been shown in the SAL that mangrove leaves can leach high amounts of organic matter (Moll et al. submitted). Therefore it is conceivable that the DON originates mainly from mangrove leaves. In the SAL highest litterfall rates were observed between November and January and lowest rates in August (Priabdi, 2003; Sukardjo, 1996). In the Paraiba do Sul River, Brazil, DON deriving mainly from sugar cane dominated the nitrogen fraction during the dry season (Krüger et al., 2004). In contrast, the Caeté Estuary, North Brazil, the

DON concentration was higher during the rainy season due to reduced mineralization rates either due to a higher percentage of recalcitrant material or a reduced residence time and microbial turnover (Schwendenmann et al., 2006). A study on organic carbon leaching from mangrove leaves has shown that the maximum concentration was observed between three and 15 days of incubation (Moll et al. submitted). The residence time of the water during the rainy season in the eastern and western lagoon is between one and three days (Holtermann et al., 2009). Leaves and nutrients can be rapidly exported during the rainy season due to the short residence time of the water. During the rainy season the DIN input from the Citanduy River and the surface runoff in the eastern area is higher than during the dry season. It is likely that during the dry season the DON input from mangrove leaf and soil leaching is high, despite the higher litterfall during the rainy season. Then, the DON concentration is probably diluted by the high precipitation or the leaves are rapidly exported before the leaching process reaches its maximum.

It has been shown earlier in the SAL that mangrove leaves do not only leach organic but also inorganic dissolved nutrients like DIN, phosphate and silicate (Moll et al., submitted). Highest phosphate concentrations from leaf leaching was observed for *Avicennia marina* and *Acanthus ilicifolius* with 5.1 to 6.5 µM g^{-1} dry weight whereas highest DIN and silicate concentrations were displayed by *A. ilicifolius* and *Derris trifoliata* (DIN: 62.3 to 66.7 µM g^{-1} dry weight; silicate: 732.1 to 1364.9 µM g^{-1} dry weight). These high leaching rates in combination with the stronger litterfall during the rainy season might also have an effect on the seasonal differences in the nutrient inventory besides differences in the nutrient-rich Citanduy discharge.

4.2 Fate of nutrients

4.2.1 Uptake by organisms

In our study almost no differences were found in the nutrient fluxes between the light, dark and lagoon water cores but fluxes varied among stations. Former studies showed consistently higher concentrations under dark conditions indicating that light has an effect on the concentrations in the water column due to nutrient assimilation by phytoplankton (Bartoli et al., 2003; e.g. DeManche et al., 1979; Kelderman et al., 1988; Spears et al., 2008). Nevertheless, many studies did not reveal significant differences between light and dark incubations, e.g. in an Australian mangrove creek (Boto et al., 1989), in the Neuse River Estuary, North Carolina (Fear et al., 2004), in Loch Leven, Scotland (Spears et al., 2008) and Lake Constance, Germany (Gerhardt et al., 2010). One reason is that both phytoplankton and phytobenthos still take up nutrients even in darkness (e.g. Bode et al., 1997; Glibert and Garside, 1992; Paasche et al., 1984; Underwood et al., 2004). Chlorophyll a values in the SAL were low in the water column as well as on the sediment surface (station 1: 1.1 ±0.6 $\mu g\ g^{-1}$; station 2: 7.2 ± 1.2 $\mu g\ g^{-1}$; Ostmann pers. comm.). The major reason for the low chlorophyll values is probably the light limitation (Yuwono et al., 2007).

In the current study, the N:P ratios were different between seasons and areas. Ratios were higher in the Citanduy, the western and central area during the rainy season (ratios: 44, 41, 36), but lower in the eastern area (ration: 8). This indicates phosphate limitation for phytoplankton and phytobenthos during the rainy season in the two areas and the river probably due to consumption by mangrove trees and bacteria. Another reason for the phosphate limitation can be sorption to Andesol soils which originates from volcanic ash and can be frequently found on Java (Jennerjahn et al., 2009 and references therein). During the dry season the ratio (between 8 and 16) was equal to or lower than the Redfield ratio.

The nutrient concentrations in the SAL were low to moderate despite the high input from the Citanduy River. Bacterioplankton can be more important for nutrient recycling than phytoplankton as its biomass can be 2 to 3 times greater (Cho and Azam, 1990). A close microbe-nutrient-plant connection seems to be an efficient mechanism to conserve nutrients in mangroves, especially when they are nutrient limited (Alongi et al., 1993). It was estimated that between 9 and 38% of the bacterial nitrogen requirements is supported by the fluxes from the sediment to the overlying water column (Robertson and Phillips, 1995).

Nutrient sinks in the SAL besides the uptake by mangrove trees is the consumption by bacteria, phytoplankton and phytobenthos. Due to the incorporation of nutrients in microalgal biomass during day and night time (Bartoli et al. 2003, Spears et al. 2008) and due to the low chlorophyll a concentrations both in the water column and on the sediment we conclude that the N missing was rather due to an uptake by bacteriobenthos, mangrove trees and denitrification and not to algal uptake.

4.2.2 Import/export

Our flux calculations for September 2009 in the Citanduy River showed that silicate and nitrogen is imported into the SAL including a possible re-import with the tides. In North Brazil nutrient-rich water was exported at low tide but transported back into the creek at the beginning of flood (Lara & Dittmar 1999, Dittmar & Lara 2001a, b). The large phosphate export during the dry season 2009 can hardly be explained. It has to be considered that the flux values represent maximum values for the rainy season. Therefore our calculations are not quantitative for the whole year as daily fluxes during the dry season are still unknown. Leaf leaching and porewater seepage are possible phosphate sources in the SAL. No accumulation of silicate and nitrogen as well as a decrease in phosphate concentrations was observed in the water column over the five year period of investigation in the current study.

5. Summary and conclusions

The nutrient input into the SAL originates mainly from the Citanduy River and therefore from the agriculture-dominated hinterland of the lagoon as well as leaching of leaves and by the Serayu River in the eastern area. Despite the high nutrient input from the Citanduy River the nutrient concentrations in the SAL are rather low to moderate but in the same range with other mangrove-fringed lagoons and rivers. Benthic recycling appears to play a minor role for the nutrient inventory of the lagoon. As no trend in the nutrient concentration over the five years of investigation was observed one major reason for the low concentrations is the short residence time of the water in the lagoon (Holtermann 2009) and therefore nutrient outwelling. Other possible nutrient sinks are mangrove trees and associated shrubs as well as uptake by microorganisms.

6. Acknowledgment

We thank Edy Yuwono and Husein Sastranegara for logistic support, Ole Morisse, Insa Pohlenga, Bushra Nasir, Matthias Birkicht, Anne Buhmann, Janina Korting and Daniel Wangprasseurt for data collection and processing and their laboratory work and Peter Holtermann for the hydrodynamic calculation. We thank Venugopalan

Ittekkot and Kai Bischof for their suggestions. Financial support by the German Federal Ministry of Education and Research (Grant Nos. 03F0391A and 03F0471A) within the SPICE (Science for the Protection of Indonesian Coastal Marine Ecosystems) program is gratefully acknowledged. This study was additionally supported by the Bremen International Graduate School for Marine Sciences (GLOMAR) that is funded by the German Research Foundation (DFG) and by the German Academic Exchange Service (DAAD).

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Figures and tables

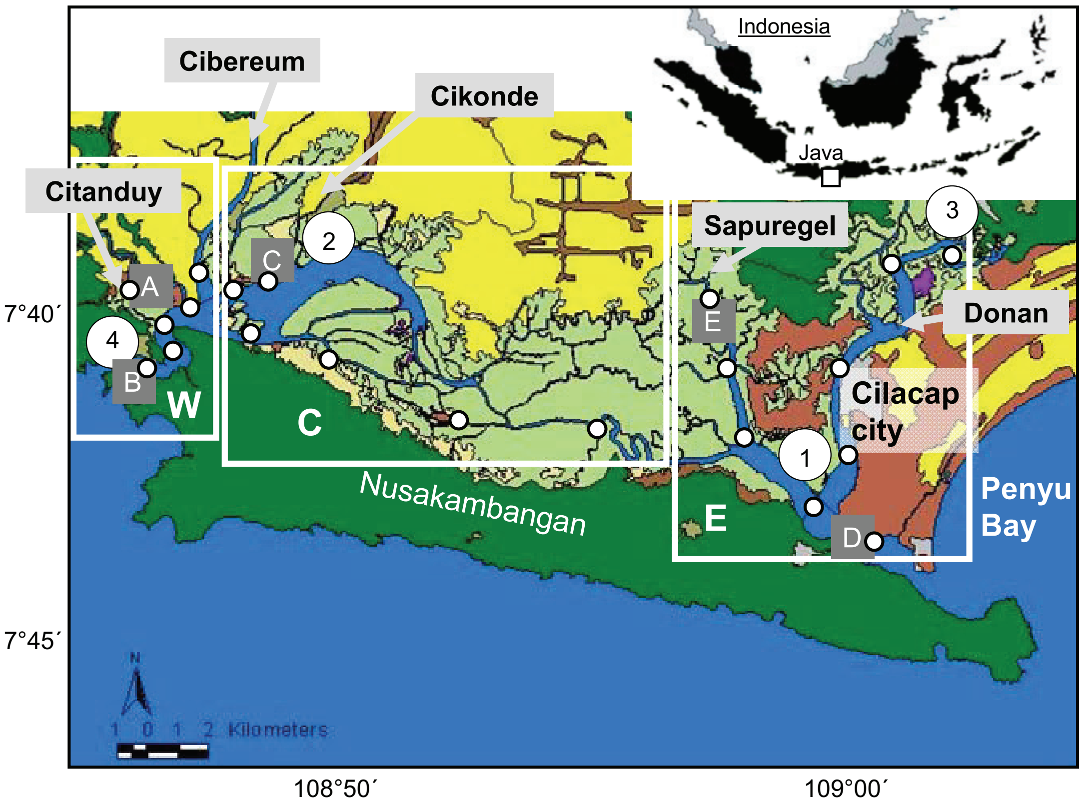

Fig. 1: Map of Segara Anakan showing the lagoon and the Indian Ocean including the sampling sites for surface water (small white circles) for the tidal variations (dark grey squares A-D) and for the incubation experiment (white circles 1-4). Yellow: agriculture (rice fields), dark green: forest, light green: mangrove, brown: urban settlements. Basis map provided by Erwin Riyanto Ardli.

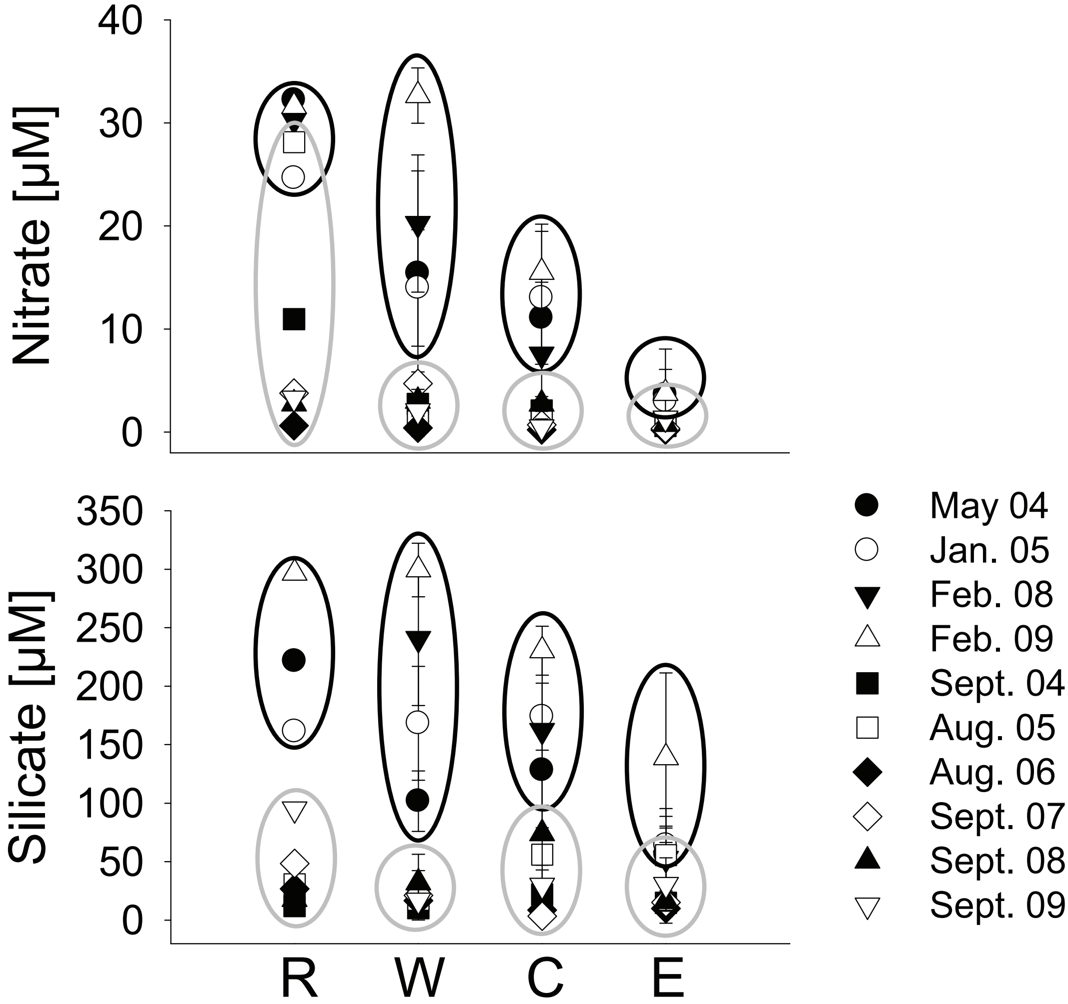

Fig. 2: Nutrient concentration during the different sampling campaigns. Grey: dry season, black: rainy season (R= Citanduy River, W= western area, C= central area, E= eastern area) including standard deviations.

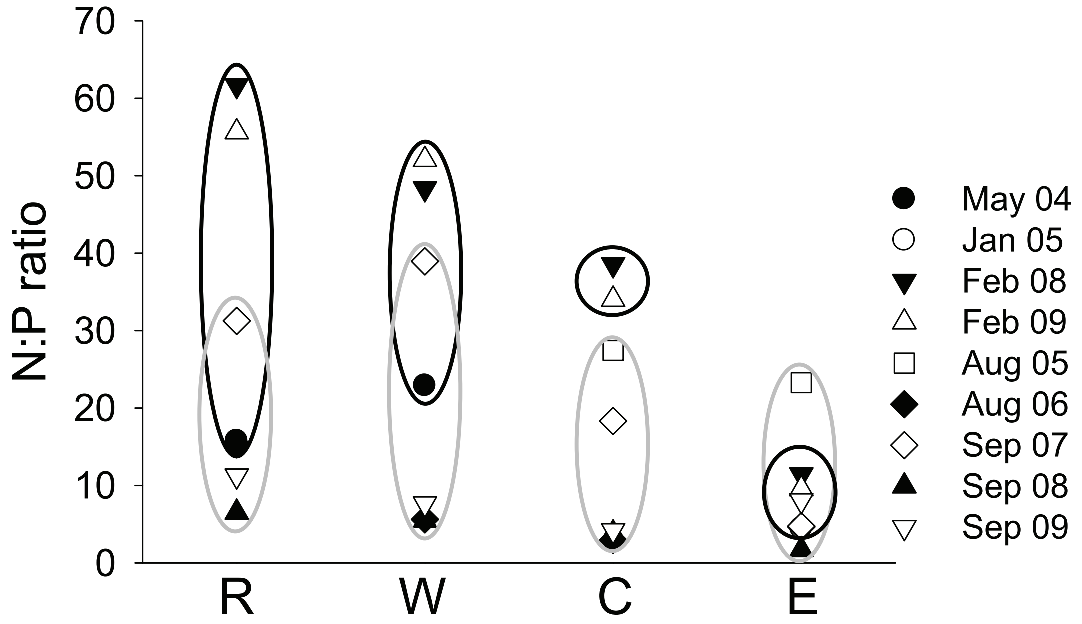

Fig. 3: The N:P ratio during the dry and the rainy season over the years. Grey: dry season, black: rainy season (R= Citanduy River, W= western area, C= central area, E= eastern area).

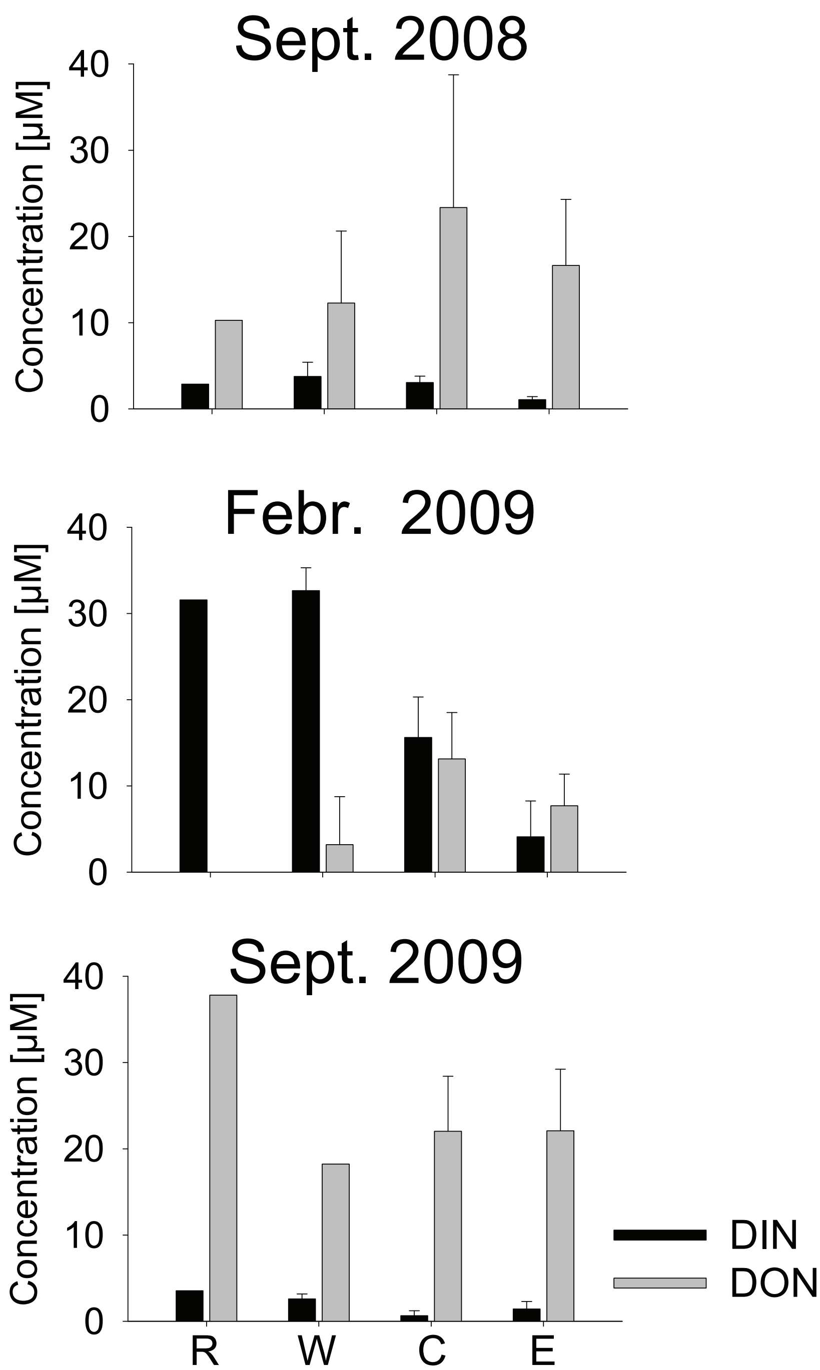

Fig. 4: Dissolved inorganic (black) and organic (grey) nitrogen concentrations during three sampling campaigns including standard deviations.

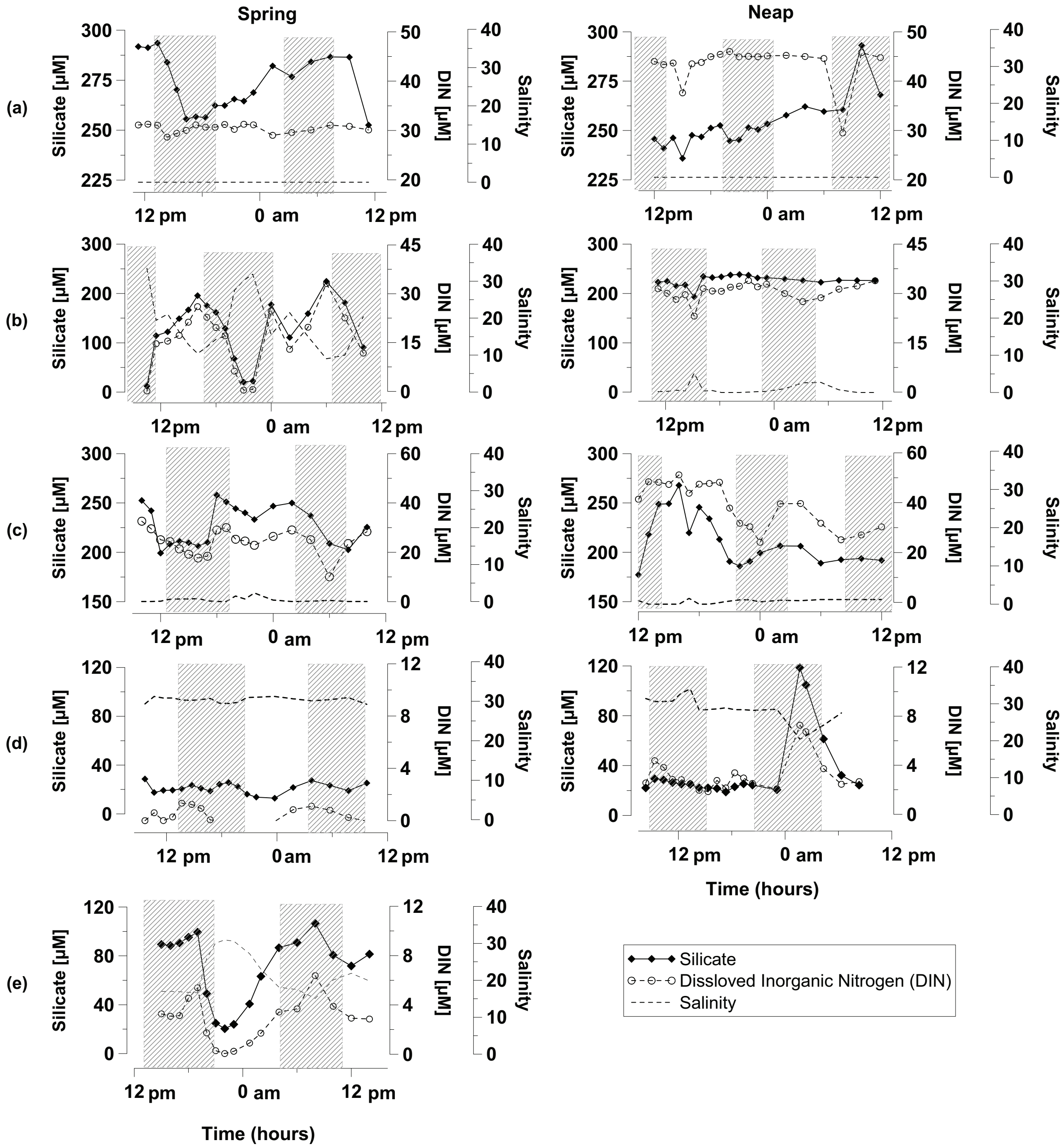

Fig. 5: Diel variation of silicate and dissolved inorganic nitrogen at the Citanduy River (a), the western outlet (b), the central lagoon (c), the eastern outlet (d) and the Sapuregel (e). Shaded bars indicate high tide.

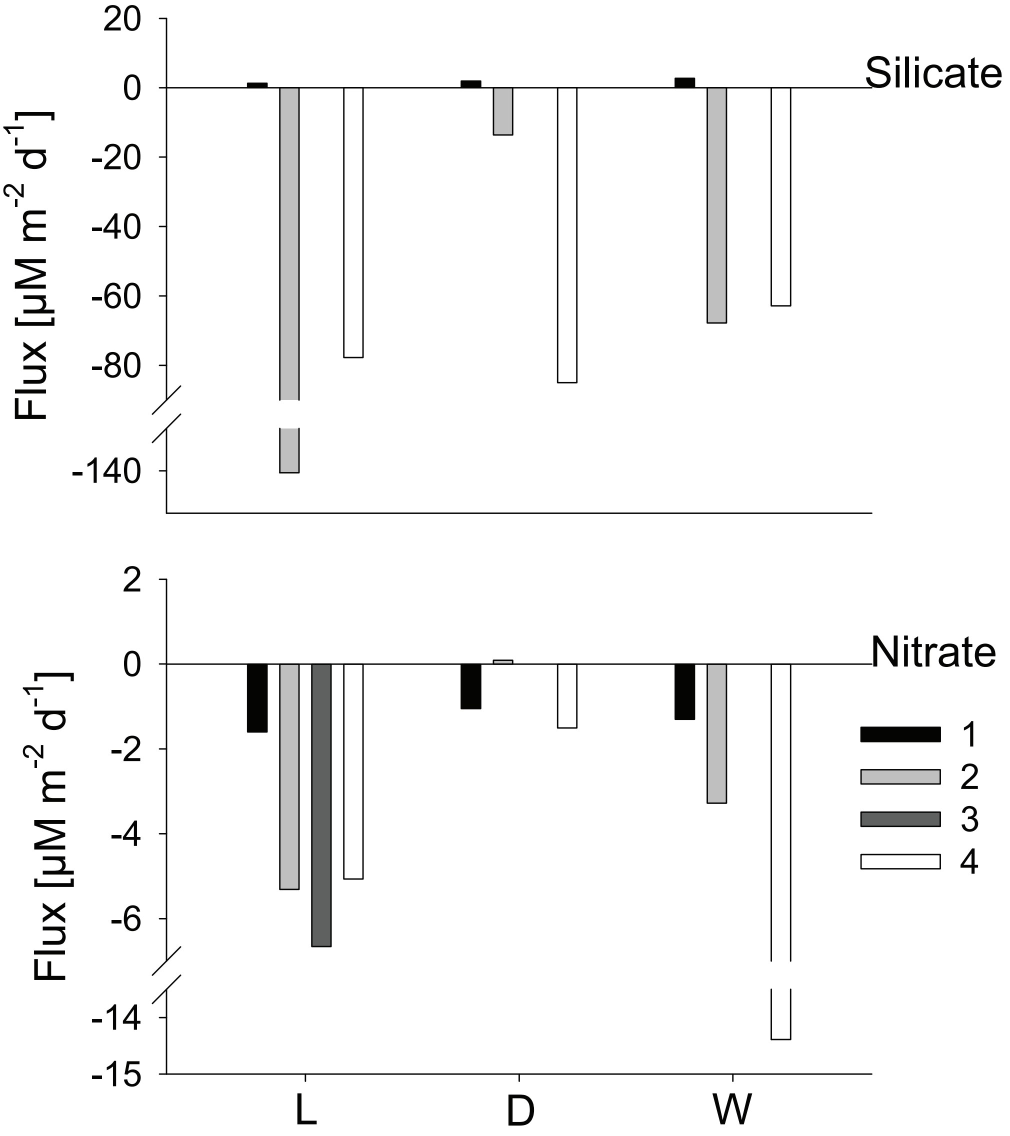

Fig. 6: Fluxes of nitrate and silicate in the three cores of the incubation experiment (L= light, D= dark, W= lagoon water). Negative fluxes denote an influx into the sediment or uptake organisms in the water column.

Tab. 1: The interactions between species, time and salinity based on a three-way ANOVA on phosphate, dissolved inorganic nitrogen, silicate and dissolved organic nitrogen (SS= sum of squares, Dgr. F= degree of freedom, MS= Means, F= test statistic of the F-test after Fisher, p= significance level, * significant parameter influencing the nutrient inventory).

		SS	Dgr F	MS	F	p
PO_4^{3-}	Year	16.53	5	3.32	88.33	0.000*
	Season	0.62	3	0.21	5.52	0.003*
	Area	0.00	1	0.00	0.05	0.803

	Year*season	0.98	2	0.49	12.98	0.000*
	Year*area	1.29	15	0.09	2.29	0.066
	Season*area	0.20	3	0.07	1.79	0.134
	Year*season*area	0.32	3	0.11	2.84	0.050
DIN	Year	14.24	5	2.85	30.54	0.000*
	Season	8.48	3	3.79	40.65	0.000*
	Area	11.37	1	8.48	90.95	0.000*
	Year*season	0.95	2	0.48	5.10	0.000*
	Year*area	5.87	15	0.39	4.20	0.003*
	Season*area	1.95	3	0.65	6.96	0.000*
	Year*season*area	1.69	6	0.28	3.02	0.001*
DIN/P	Year	4.56	5	0.91	7.63	0.000*
	Season	5.28	3	1.76	14.72	0.000*
	Area	6.32	1	6.32	52.86	0.000*
	Year*season	0,20	15	0.10	0.82	0.207
	Year*area	5.74	2	0.38	3.20	0.007*
	Season*area	2.08	3	0.69	5.79	0.000*
	Year*season*area	1.34	3	0.45	3.75	0.003*
$Si(OH)_4^-$	Year	7.36	5	1.47	19.59	0.004*
	Season	2.71	3	0.90	12.04	0.023*
	Area	5.84	1	5.84	77.71	0.000*
	Year*season	0.41	2	0.33	2.74	0.127
	Year*area	4.98	15	0.21	4.42	0.032*
	Season*area	1.65	3	0.55	7.30	0.001*
	Year*season*area	0.46	5	0.09	1.22	0.156

Tab. 2: Estimated daily fluxes [mol d^{-1}] of nutrients in the SAL during the rainy season. Negative fluxes indicate export to the ocean.

		Citanduy River	Western outlet	Eastern outlet
Spring tide	$Si(OH)_4$	9.7×10^6	-2.7×10^6	-0.2×10^6
	PO_4^{3-}	1.4×10^4	-9.1×10^4	-0.02×10^4
	DIN	10.8×10^5	-3.1×10^5	0.07×10^5
Neap tide	$Si(OH)_4$	6.9×10^6	-4.0×10^6	-0.06×10^6
	PO_4^{3-}	0.5×10^4	-0.7×10^4	-0.01×10^4
	DIN	11.6×10^5	-4.8×10^5	-0.4×10^5

Tab. 3: Nutrient [µM] and chlorophyll a [µg l^{-1}] concentrations in lagoons and creeks (ds: dry season, rs: rainy season). Reference: *: current study, 1: Yuwono eta l. 2007; 2: Hung and Kuo 2002; 3: Dittmar and Lara 2001, Lara and Dittmar 1999; 4: Ovalle et al. 1999, 5: Silva et al. 2001, Krüger et al. 2004, 6: Herrera-Silveira 1996; 7: Markou et al. 2007, 8: Welter et al. 2005, 9: Vink et al. 2007.

Location		**Vegetation**	**season**	**NO_3^-**	**NO_2^-**	**NH_4^+**	**DIN**	**DON**	**$Si(OH)_4$**	**$PO4_3^-$**	**chl. a**	**Reference**
Indonesia, Java	Citanduy	Mangrove	ds	3,3	0,1	~0	3,4	24,0	54	0,3	0,2	*
(SAL)			rs	30,9	0,5	~0	31,4	-	297	0,5	2,7	
(2007 - 2009)	Area E		ds	0,8	0,3	~0	1,1	15,2	20,6	0,3	0,1	
			rs	11,5	0,5	~0	2,9	3,2	196,2	0,3	4,4	
	Area C		ds	1,3	0,3	~0	1,6	22,7	35,7	0,4	0,2	
			rs	2,5	0,5	~0	12,0	13,1	95,8	0,3	6,8	
	Area W		ds	3,3	0,3	~0	3,6	19,4	23,4	0,4	0,1	
			rs	26,4	0,4	~0	26,8	7,7	270	0,5	1,5	
Indonesia, Java	Citanduy	Mangrove	rs	32,2	3,8	4,4	40,3			<0,1	1,8	1
(SAL)	Area W			11,8	1,1	3,1	16			<0,1	2,8	
(May 2004)	Area C			11,3	2,1	2,6	15,9			<0,1	4,6	
	Area E			4,3	0,9	2,3	7,5			<0,1	6,1	
Southwest Taiwan	Chiku Lagoon	Mangrove	ds				14,35	18,75		2,6		2
			rs				9,17	19,67		2,9		
North Brazil	Caeté Estuary	Mangrove	ds	0 - 6		2 - 15		12 - 55	100 - 250	1 - 5		3
			rs	1 - 16		4 - 20		16 - 30	90 - 260	0,5 - 4,5		
East Brazil	Canavieiras (coast)	Mangrove	end of ds	1,2		1		0,6	1,1	0,3	0,2	4
	Cabralia (coast)	Mangrove		0,5		1		0,8	1,4	1,0	0,2	
	Caravelas (coast)	Mangrove		0,3		1,5		0,8	1,6	0,4	0,2	
	Esp. Santo (coast)	Mangrove		<0,1		0,9		1,3	3,2	0,3	1	
Brazil	Paraiba do Sul River	Sugar cane	annual mean	7 - 57	0,1 - 0,5	0,3 - 6,7	24,5 - 60,9	4,9 - 86	67,4 – 174,0	0,4 - 1,66		5
Mexico	Celestun Lagoon	Mangrove	annual mean	8,1	0,3	6,1			62,5	1,2		6
North Greece	Vistonis Lagoon		annual	3,5	0,2	13,8				1,2	39,1	7

			mean				
USA	Arizona	desert scrub	summer	69,3	62,1		8
			winter	22,8	27,1		
Southeast Australia	Kileys Run	Grass	ds	9,3 - 28,6	5 - 10,7	0,6	9
	Red Hill	Pines		242,7 - 302	12,1 - 15,7	0,3	

Tab. 4: Nutrient fluxes [µmol m^{-2} d^{-1}] using different methods in tropical and temperate areas (L= light, D= dark, W= lagoon water). Reference: *: current study, 1: Davis et al. 2001; 2: Alongi 1991; Alongi et al. 1993; 3: Alongi 1996; 4: Eyre and Ferguson 2005; 5: Friedrich et al. 2002; 6: Gardner and McCarthy 2009; 7: Fear et al. 2004; 8: Bartoli et al. 2003, 9: Spears et al. 2008; 10: Rizzo et al. 1992; 11: Kelderman et al. 1988; 12: Boynton and Kemp 1985; 13: Moore et al. 1991; Reddy et al. 1996.

Location		treatment	NH_4^+	NO_3^-	PO_4^{3-}	Si	Method	Reference
Indonesia, Java	Station 1	L	~0	-1,6	~0	1,3	Sediment core	*
		D	~0	-1,1	~0	2		
		W	~0	-1,3	~0	2,7		
	Station 2	L	~0	-5,3	~0	-140,5		
		D	~0	0,1	~0	-13,6		
		W	~0	-3,3	~0	-67,8		
	Station 3	L	~0	-6,7	~0	~0		
		D	~0	~0	~0	~0		
		W	~0	~0	~0	~0		
	Station 4	L	~0	-5,1	-0,06	-77,7		
		D	~0	-1,5	-0,03	-845		
		W	~0	-14,4	-0,54	-62,9		
Florida	Southern Everglades		-754 to -158	-	-199 to -50	-	mangrove enclosure	1
Papua New Guinea	Fly Delta		-63360 to 1248	-	-1680 to -168	-77472 to 46728	bell jars	2
Australia	Coral Creek		-96 to 1776		-28 to 96	-720 to 4920	sediment core	3
East Australia		L	-792 to 3936	-3120 to 1536	-	-	sediment core	4
		D	-312 to 4920	-3720 to 2640	-	-		
North Western	Danube delta front		950	-80	-	1845	benthic chamber	5

Black Sea								
Florida			3777	56	84	-	core incubation	6
USA, North Carolina	Neuse River Estuary	D	-165	-24	-6	-	sediment cores, incubation	7
		L	339	-69	21	-		
Sweden	Tjarno	D	1462	-1538	-	365 to 2570	incubation	8
		L	46	-2114	-	-24 to 154		
Scotland	Loch Leven	D	-1386 to 1220	-	-11 to 42	-1051 to 8084	incubation	9
		L	-444 to 388	-	-21 to 116	-1248 to 11715		
USA, North Carolina	Neuse River	L	72 to 288	-	-	-	sediment core	10
		D	312 to 528	-	-	-		
Netherlands	Lake Grevelingen	L	-	-	126	333	bell jars	11
		D	-	-	874	2861		
USA	Chesapeake Bay		854 to 19704	-2880 to 6912	-120 to 960	-	in situ chamber	12
Florida, USA	Lake Apopka		1386	-	11 to 18	-	sediment core	13

Fate of organic matter derived from mangroves and from an agriculture-dominated hinterland in the Segara Anakan Lagoon, Java, Indonesia

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Abstract

The sources, sinks and diagenetic status of organic matter (OM) in the mangrove-fringed Segara Anakan Lagoon were investigated by using the C/N ratio, stable isotope composition and total hydrolysable amino acids (THAA). The lagoon receives a high sediment input from an agriculture-dominated hinterland through the Citanduy River in the West with total suspended matter (TSM) concentrations of up to 1600 mg l^{-1}. The sediment in the lagoon contained between 0.1 and 1.5% organic carbon (C_{org}) during the rainy season and between 0.9 and 1.5% during the dry season whereas in TSM the values ranged between 1.4 and 2.9% and between 1.2 and 2.2%, respectively. Amino acids accounted for 17.4-29.6 % of C_{org} (THAA-C) in the TSM and for 2.5-15.7 % in the sediment. A strong east-west gradient was observed in the carbon and nitrogen stable isotope composition of the TSM and the sediment in the lagoon. Most of the organic matter in the lagoon derived from terrestrial sources, mainly from anthropogenic sources like rice fields in the hinterland but also from natural sources like mangroves. The suspended matter either accumulates in the

lagoon where it undergoes substantial degradation or it can be outwelled to the Indian Ocean, mainly through the western outlet.

Keywords

Amino acids, total suspended matter, sediment, carbon, nitrogen, isotopic composition, mangroves, Segara Anakan Lagoon

1. Introduction

Mangroves are highly productive ecosystems along tropical coastal areas with net primary production rates of up to 20-50 t C ha^{-1} y^{-1} (Clough, 1998; Jennerjahn and Ittekkot, 2002; Kennedy et al., 2004). Due to the location of mangroves between the land and the ocean the particulate material can originate from sediment, plant detritus and marine particulate organic matter (OM) (Bouillon et al., 2007b). The OM produced either accumulates in the mangrove sediments or is exported as detrital material to adjacent ecosystems (Bouillon et al., 2007a; Bouillon et al., 2003; Bouillon et al., 2007b; Dittmar and Lara, 2001; Kennedy et al., 2004) where it promotes the food webs (Odum and Heald, 1975; Rodelli et al., 1984). The outwelling of carbon is influenced by the geomorphology, water depth, and tidal characteristics of the system (Lee, 1999).

It has been shown that the C/N ratio, the stable isotope composition of carbon and nitrogen and amino acids provide useful information in order to determine the sources and diagenetic status of OM (Bouillon et al., 2007a; 2002; Cowie and Hedges, 1992; Duarte, 1992; Jennerjahn and Ittekkot, 1997; Lee et al., 2000; Sturgis and Murray, 1997; Unger et al., 2005). The C/N ratio is known as a source indicator even though the use of this ratio is not straightforward as OM derived from different sources may have variable C/N ratios and different pathways of nitrogen mineralization (Burdige, 1991; Müller, 1977). $\delta^{13}C_{org}$ can be used as a source indicator as values differ between terrestrial and marine sources (Bouillon et al., 2007a; Kennedy et al., 2004; Rau et al., 1989; Sweeney and Kaplan, 1980). This parameter also shows the degree of OM degradation and anthropogenic inputs like sewage (Rau et al., 1981; Sweeney and Kaplan, 1980; Van Dover et al., 1992; Wankel et al., 2006). Compounds like lignin or lipids are more resistant than the easily degradable total hydrolysable amino acids (THAA) and hydrocarbons as the remaining OM after bacterial degradation is enriched in ^{13}C and ^{15}N (Böttcher et al., 1998; Freudenthal et al., 2001; Sweeney and Kaplan, 1980; Uhle et al., 2007). THAA and total hydrolysable hexosamines (THHA) occur in proteins of all living organisms (Dauwe et al., 1999; Lee and Cronin, 1982; Lee et al., 2000; Unger et al., 2005). THAA make up a major fraction of labile OM as they account for 40 – 90% of the nitrogen in sediments and suspended matter (Haugen and Lichtentaler, 1991; Henrichs and Farrington, 1987; Lee and Cronin, 1984; Müller et al., 1986). Due to their lability relative to bulk OM it is an important proxy for degradation (e.g. Cowie and Hedges, 1992; Dauwe et al., 1999; Gupta and Kawahata, 2000; Haugen and Lichtentaler, 1991; Keil and Fogel, 2001; Lee and Cronin, 1982).

This study was conducted over a period of five years to investigate the sources and the fate of OM in the mangrove-fringed Segara Anakan Lagoon (SAL). This lagoon decreases rapidly due to its high sediment input. A combination of the C/N ratio, the isotopic composition as well as THAA and THHA was used to obtain information on the sources and to differentiate between natural sources like mangroves and marine OM and anthropogenic sources like agriculture as well as its diagenetic status.

2. Material and Methods

2.1 Study area

The SAL (Fig. 1), which is located in south central Java (108°46′E – 109°03′E, 7°35′S – 7°48′S), is threatened by high sediment input mainly from the Citanduy River (annual freshwater discharge: dry season 171 $m^3 s^{-1}$, rainy season 283 $m^3 s^{-1}$) in the western lagoon. This led to a rapid decrease in lagoon area and depth in the last decades (Jennerjahn et al., 2009a; Purba, 1991; White et al., 1989; Whitten et al., 2000; Yuwono et al., 2007a). The sedimentation increase was mainly due to the unsustainable land-use practices in the hinterland (Yuwono et al., 2007b). Additionally to the sediment input, the lagoon is endangered by the conversion of mangrove area into rice fields and aquaculture which was estimated to be ~52% since 1978 (Ardli and Wolff, 2009). The sediment load was estimated to be $6*10^6$ $m^3 yr^{-1}$ and is discharged into the Indian Ocean through the western lagoon (Yuwono et al., 2007a). The central and western part of the lagoon are very shallow (average depth during the last 2 years: west 3.8 m, central 2.1 m) whereas the eastern part is slightly deeper with 4.9 m.

Insert Fig. 1

2.2 Sampling

Sampling campaigns in the SAL were performed in May and October/November 2004, January 2006, September 2007, February and September 2008 and February and September 2009. Water samples were taken at 23 stations in the lagoon (one in the Citanduy River, six in the western area, seven in the central area and nine in the eastern area). Additionally, five stations were sampled in February 2009 in the adjacent Penyu Bay.

2.2.1 Water and sediment sampling

A PE-container was filled with surface water and stored dark and cool until return to the laboratory where the water was filtered on pre-weighed and combusted Whatman GF/F filters (particle retention: 0.7 µm). Sediment samples were taken with an Ekman-grab of which ~15 g of sediment surface were put into pre-annealed glass vials and dried at 40°C. The suspended matter on the filter and the sediment samples were analyzed for organic carbon (C_{org}), total nitrogen (N), isotopic composition ($\delta^{13}C_{org}$ and $\delta^{15}N$) and amino acids.

2.2.2 Sample analysis

Particulate carbon (total and organic) and nitrogen were analyzed using a Carlo-Erba NA 2100 Elemental Analyzer. For analyzing the isotopic composition of C_{org} and N the Thermo Finnigan Delta^{plus} mass spectrometer combined with a Carlo Erba Flash EA 1112 elemental analyzer via ConFlo III interface was used (analytical errors for C_{org} <0.1%, for N <0.01, for $\delta^{13}C$ and for $\delta^{15}N$ <0.2‰). THAA and THHA were quantified by the low pressure ion exchange chromatography *Biochrome B30* by hydrolysing the TSM and sediment samples with 6 N HCl. Afterwards the aliquotes were evaporated, filled with distilled water and evaporated again (analytical errors for the amino acids and hexosamines < 6%).

2.3 Statistical analysis and calculations

The reactivity index RI was calculated as the ratio of aromatic THAA and the non-protein THAA (β-Ala and γ-Aba).

3. Results

3.1 TSM

The TSM concentration was much higher during the rainy season compared to the dry season (Fig. 2). During the rainy season a higher TSM concentration was observed in the Citanduy and the western area (up to 1600 mg l^{-1}) but almost no differences were found between the four areas during the dry season (average 29.4 ± 17.2 mg l^{-1}). The TSM load in Penyu Bay was 24.0 ± 11.6 mg l^{-1} in February 2009.

Insert Fig. 2

3.2 C_{org} and N content of the sediment and the TSM

The organic carbon content ranged between 0.13 and 1.51% in the sediment and 1.17 and 2.28% in the TSM (Tab. 1). More organic carbon was found in the western area both in the TSM and in the sediment. No differences were found between the dry and the rainy season except for the sediment in the Citanduy. There, the C_{org} content was significantly lower during the rainy season. The nitrogen content ranged between 0.01 and 0.11% in the sediment and was higher in the TSM with 0.15 and 0.37%.

Insert Tab. 1

3.3 C/N ratios of sediment, TSM, mangrove leaves, rice plants and rice soils

In the Citanduy and the western area the C/N ratios were higher during the dry season than during the rainy season both in the sediment and the TSM. No differences were found for the central and eastern lagoon. The mean C/N ratios of sediments from the four sampling areas were between 11.6 and 20.6 and therefore higher compared to the TSM (between 7.9 and 9.8). No differences in the ratios of the TSM were found between the Citanduy River and the three lagoon areas.

The C/N ratios of brown leaves on the sediment surface differed between species and ranged between 28.1 and 45.2 for *Avicennia alba, Aegiceras corniculatum, Acanthus ilicifolius*, *Sonneratia alba* and *Xylocarpus granatum* and were higher for *Bruguiera gymnorrhiza* with 75.1. The C/N ratio in rice plants was 31.2 and ranged between 10.8 and 12.7 in rice field soils.

3.4 Isotopic composition of sediment, TSM, mangrove leaves, rice plants and rice soils

The isotopic composition both for carbon and nitrogen in the sediment surface were lower in the eastern area ($\delta^{13}C_{org}$ -26.9 ± 0.3‰; $\delta^{15}N$ 3.1 ± 0.6‰) and increased towards the western area ($\delta^{13}C_{org}$ -25.8 ± 0.2‰; $\delta^{15}N$ 4.2 ± 0.5‰) and the Citanduy River ($\delta^{13}C_{org}$ -25.8 ± 0.3‰; $\delta^{15}N$ 4.3 ± 0.1‰; Fig. 3). Except for the Citanduy River higher nitrogen isotopic compositions were found during the rainy season but differences were not significant. Much lower $\delta^{13}C$ values were found for rice plants and various mangrove species, being lowest for *Aegiceras corniculatum, Bruguiera gymnorrhiza* and *Xylocarpus granatum*. Soil from rice fields had $\delta^{13}C_{org}$ values of -26.5 ± 1.3‰ and $\delta^{15}N$ values of 4.9 ± 1.9‰.

Insert Fig. 3

Higher $\delta^{15}N$ and lower $\delta^{13}C_{org}$ values were found in the TSM of the eastern area ($\delta^{13}C$ -26.7 ± 1.3‰; $\delta^{15}N$ 5.6 ± 1.1‰, Fig. 4) and ^{13}C increased with decreasing isotopic nitrogen signatures towards the western area. There, the data showed higher variations between sampling times ($\delta^{13}C$ -25.3 ± 2.1‰; $\delta^{15}N$ 3.5 ± 3.8‰). Both $\delta^{15}N$ and $\delta^{13}C$ values were slightly lower during the dry season but changes were not significant.

Insert Fig. 4

The C/N ratio increased with decreasing $\delta^{13}C_{org}$ values towards the east (Fig. 5). Highest C/N ratios in combination with lowest $\delta^{13}C_{org}$ values were found in rice plants and rice plant soils.

Insert Fig. 5

3.5 Amino acids in the sediment and the TSM

The THAA content in the TSM ranged between 6.3 and 12.9 mg g^{-1} and in the sediment between 0.9 and 4.0 mg g^{-1}. THHA contents ranged between 0.8 and 1.1 mg g^{-1} in the TSM and between 0.2 and 0.8 mg g^{-1} in the sediment. The THAA-mol% was higher in the central and eastern area in the TSM during the rainy season 2009 than in the sediment (Tab. 2). No spatial or temporal gradient was observed for the THAA-concentrations during the dry season which ranged between 126 and 155 mol% in the TSM and between 58 and 134 mol% in the sediment. The organic carbon contributed by THAA was lower during the rainy season. The THAA-C% was higher with 20.6 ± 9.6 (Feb. 2009) and 25.9 ± 8.5 (Sep. 2009) in the TSM than in the sediment (average Feb. 2009: 7.9 ± 2.1; Sep. 2009: 13.8 ± 10.2). The THAA-N% displayed the same pattern with 39.1 ± 6.4 (Feb. 2009) and 44.0 ± 7.3 (Sep. 2009) in the sediment and 47.3 ± 22.5 (Feb. 2009) and 65.9 ± 16.8 (Sep. 2009) in the TSM. The RI was higher in the TSM (2.3 to 14.9) than in the sediment (1.7 to 2.9).

Insert Tab. 2

4. Discussion

4.1 Sources of sediment and TSM

The average C/N ratio ranged between 11 and 23 in the sediment and displayed higher ratios in the eastern lagoon whereas the average ratio in the TSM ranged between 7 and 14. There, no spatial gradient was observed. The ratio of marine phytoplankton is known to be between 5 and 15 (Bouillon et al., 2003; Duarte, 1992; Meyers, 1997) whereas terrestrial sources have a wide range of between 12 and 400 which decreases during diagenesis (Meyers, 1997; Nedwell, 1999; Uhle et al., 2007). The sediment C/N ratio in the current study is lower than those found for mangrove leaves in the SAL as well as in the literature (20-262) (Meyers, 1997; Rao et al., 1994, Herbon et al., submitted) but in the same range with mangrove sediments in the Paraiba do Sul river mouth with 11.7 (Jennerjahn and Ittekkot, 1997). It has been shown in various studies that sorption of nitrogen to particulate material and OM degradation due to bacterial processing can lead to a decrease in the C/N ratio (e.g. Burdige, 1991; Ferguson et al., 2007; Hedges et al., 2000; Meybeck, 1982; Müller, 1977; Nedwell, 1999; Rao et al., 1994). In the Citanduy River, the western and the central area the sediment grain size is dominated by fine-grained particles. Therefore, it is likely that the C/N ratios in the river and the two areas are higher due to adsorption of ammonium. The average C/N ratios showed that the eastern lagoon receives more terrestrial input than the Citanduy River, the western and the central area.

The $\delta^{13}C_{org}$ values in the sediment of the Citanduy River and the three lagoon areas ranged between -25 and -28‰ which was lower than those for brown mangrove leaves and rice plants (-27 and -30‰). The isotopic carbon composition showed high variations both in the TSM and in the sediment in the central (-24 to -28‰) and the western (-21 to -28‰) area. $\delta^{13}C_{org}$ values from mangrove leaves are known to be between -24 and -30‰ (Bouillon et al., 2008; Bouillon et al., 2007a; Kennedy et al., 2004; Marguillier et al., 1997; Rodelli et al., 1984) and for marine OM between -17 to -23‰ (Bouillon et al., 2008; Haese, 2006 and references therein; Rodelli et al., 1984). It has been shown for other mangrove-fringed areas like in Australia, the Philippines or Vietnam that mangrove leaf litter is the major component of deposited OM (e.g. Kennedy et al., 2004; Robertson et al., 1992; Woodroffe et al., 1988). The isotopic composition in the sediment in the current study displayed a spatial gradient. Our data showed that the SAL is almost entirely affected by the input of terrestrial material from rice fields in the hinterland and therefore anthropogenic sources as well as of natural sources like mangrove leaves. The increase in the C/N ratio in combination with a decrease in the $\delta^{13}C_{org}$ towards the east shows that the eastern lagoon is more influenced by mangrove-derived OM compared to the western lagoon, which receives more OM from rice fields. It is surprising that no effect from the Indian Ocean was observed in the eastern lagoon even though salinities of ~30 were measured also in this area (Moll et al., submitted). The TSM in the western lagoon during the dry season 2009 and in the Penyu Bay is influenced by the Indian Ocean. Despite the high riverine input in the western area the salinity during the dry season was > 30. This, as well as the lower $\delta^{13}C_{org}$ values down to -21.8‰, indicate a marine influence in the western lagoon during the dry season when the river discharge is low. Marine dissolved OM shows a stronger sorption to suspended matter than terrigenous OM

(Keil and Fogel, 2001; Uhle et al., 2007). As the Citanduy River discharges high loads of suspended matter it is conceivable that marine dissolved OM had a stronger sorption to this TSM at the western outlet.

$\delta^{15}N$ values in the sediment ranged between 2 and 4‰ in the eastern lagoon and between 3 and 5‰ in the Citanduy River and the western lagoon. TSM values were between -1 and 8‰ and did not show a spatial gradient. The OM increases in ^{15}N and ^{13}C after degradation as a consequence of bacterial metabolism. This is comparable to the general observation in food webs with an enrichment of heavier isotopes in higher trophic levels (Freudenthal et al., 2001; Macko and Estep, 1984). The lower isotopic values in the eastern lagoon can either occur due to fixation of atmospheric nitrogen in mangroves or due to a stronger pollution by sewage from households. It has been shown that organisms had a lower $\delta^{15}N$ at sewage-polluted sites than from non-polluted sites in South California (Rau et al., 1981). Especially $\delta^{15}N$ values can be used to distinguish between sewage ($\delta^{15}N$ averaging ~3‰) and marine-derived material (averaging ~7‰) (Tucker et al., 1999; Van Dover et al., 1992). Therefore, it is possible that the SAL might be affected by the input of sewage waters which alters the isotopic composition in the sediment.

The bulk C/N and isotope values for the sediment and TSM suggest that mainly terrigenous materials are OM sources in the SAL. Nevertheless, it has to be considered that the $\delta^{13}C_{org}$ values at the eastern outlet can vary by up to 4‰ between high and low tide (Santoso pers. comm.) which complicates the source identification by the use of stable isotopic compositions. Additionally, the bulk C/N and isotopic composition do not provide detailed information on individual carbon sources or diagenetic pathways. For this, other compound-specific parameters like the isotopic composition or the chiral structure of amino acids would be necessary (Keil and Fogel, 2001; Macko et al., 1994; McClelland et al., 2003; Uhle et al., 2007).

4.2. Organic matter degradation and fate of suspended material in the SAL

The mean C/N ratios were higher in the sediment than in the TSM in the SAL. Increasing C/N ratios with water depth indicates a preferential transformation of nitrogen compounds (Burdige, 1991; Cowie and Hedges, 1994; Müller et al., 1986). Therefore, the sediment in the SAL is more degraded than the TSM.

The $\delta^{15}N$ values showed high variability in the TSM (-1 to 8‰) compared to the sediment (2-5‰). $\delta^{15}N$ of surface marine sediments range between 4 and 9‰ (Tucker et al., 1999) which is at the upper end of the range found in the current study. $\delta^{15}N$ of particulate matter increases during OM degradation (Holmes et al., 1999) which might indicate that the eastern lagoon has more degraded TSM than the western lagoon.

The total THAA content and the THAA-C% were higher in the TSM than in the sediment. The amount of THAA-C% in the current study is in the same range of other coastal sediments with 7 to 45% (Aufdenkampe et al., 2001 and references therein; Henrichs and Farrington, 1987; Jennerjahn et al., 1999; Lee and Cronin, 1982; Wakeham et al., 1993). The THAA-N made up to 38-79% of the total nitrogen in the TSM and sediments in the SAL. These values were higher than those reported for the equatorial Pacific with ~25% (Lee et al., 2000) but in the same range with those in the São Fransisco River in East Brazil, the Kallada River in India and the Brantas River in Indonesia (Jennerjahn and Ittekkot, 1997, 1999; Jennerjahn et al., 1999). It has been shown earlier that the concentration of THAA decreases due to a preferential degradation (Gupta and Kawahata, 2000; Haugen and Lichtentaler, 1991; Rosenfeld, 1979).

The RI values were lower in the sediment (1.7 to 2.4) than in the TSM (2.3 to 14.9). The reactivity of the sedimentary OM was in the range with those found in the Brantas River (2.9) and in a mangrove area in the Paraiba do Sul river mouth (2.3). RIs reported for TSM were between 1.5 and 2.5 in the Kallada River and 15.1 in the Brantas River (Jennerjahn and Ittekkot, 1997; Jennerjahn et al., 2009b). The total THAA content in the TSM was higher than in the sediment probably due to bacterial uptake on the sediment surface. Such consumption leads to a decrease in the aromatic THAA and an increase in the non-protein THAA content. The lower RI, the lower THAA content and the lower THAA-C% in the sediment compared to the TSM as well as the higher C/N ratio indicate that the OM in the sediment of the SAL has undergone substantial degradation.

5. Summary and conclusions

The TSM as well as the sediment derive both from natural and anthropogenic sources in the SAL. Our data showed that terrestrial OM is the main source for the sediment and the TSM in the SAL. In the western lagoon this terrestrial matter mainly derives from the rice fields in the agriculture-dominated hinterland whereas in the eastern lagoon receives more input from natural sources like mangrove leaves. However, the western outlet was affected by the Indian Ocean during the dry season 2009 as shown by the low $\delta^{13}C_{org}$ values in combination with high salinities. By using a combination of C/N ratios, isotopic compositions and amino acids we have shown that the OM in the western lagoon derives from rice fields and in the eastern lagoon from mangrove leaves and that this material either accumulates in the sediment where it undergoes severe degradation or it is outwelled into the Indian Ocean. Only little amounts of the TSM was transported from the lagoon into the adjacent Penyu Bay. However, it is known that most of the suspended matter is discharged from the Citanduy River through the western outlet.

Acknowledgement

Data collected between May 2004 and August 2006 and used in this investigation were supplied by Ole Morisse, Insa Pohlenga and Bushra Nasir. Thanks are given to Edy Yuwono and Husein Sastranegara for their help with organizational matters in the field and in the laboratory in Indonesia and Dorothee Dasbach and Christina Staschok for the analysis in the laboratories in Germany. We thank the students who contributed to field data acquisition and processing both from UNSOED and Bremen University, especially Anne Buhmann and Daniel Wangprasseurt. We thank Venugopalan Ittekkot and Kai Bischof for their suggestions. This study is supported by the Bremen International Graduate School for Marine Sciences (GLOMAR) that is funded by the German Research Foundation (DFG). Financial support by the German Federal Ministry of Education and Research (Grant Nos 03F0391A and 03F0471A) within the SPICE (Science for the Protection of Indonesian Coastal Marine Ecosystems) program is gratefully acknowledged.

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Figures and tables

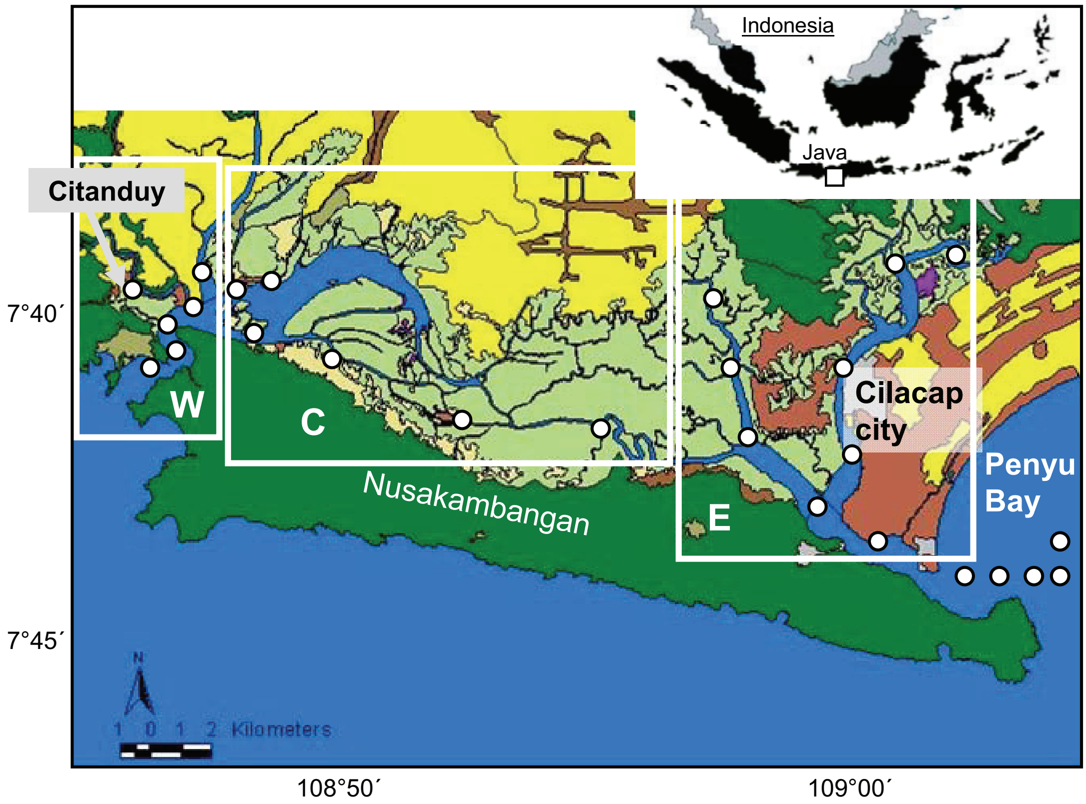

Fig 1: Map of Segara Anakan including the 28 sampling sites (white circles). Yellow: agriculture (rice fields), dark green: forest, light green: mangrove, brown: urban settlements. Basis map provided by Erwin Riyanto Ardli.

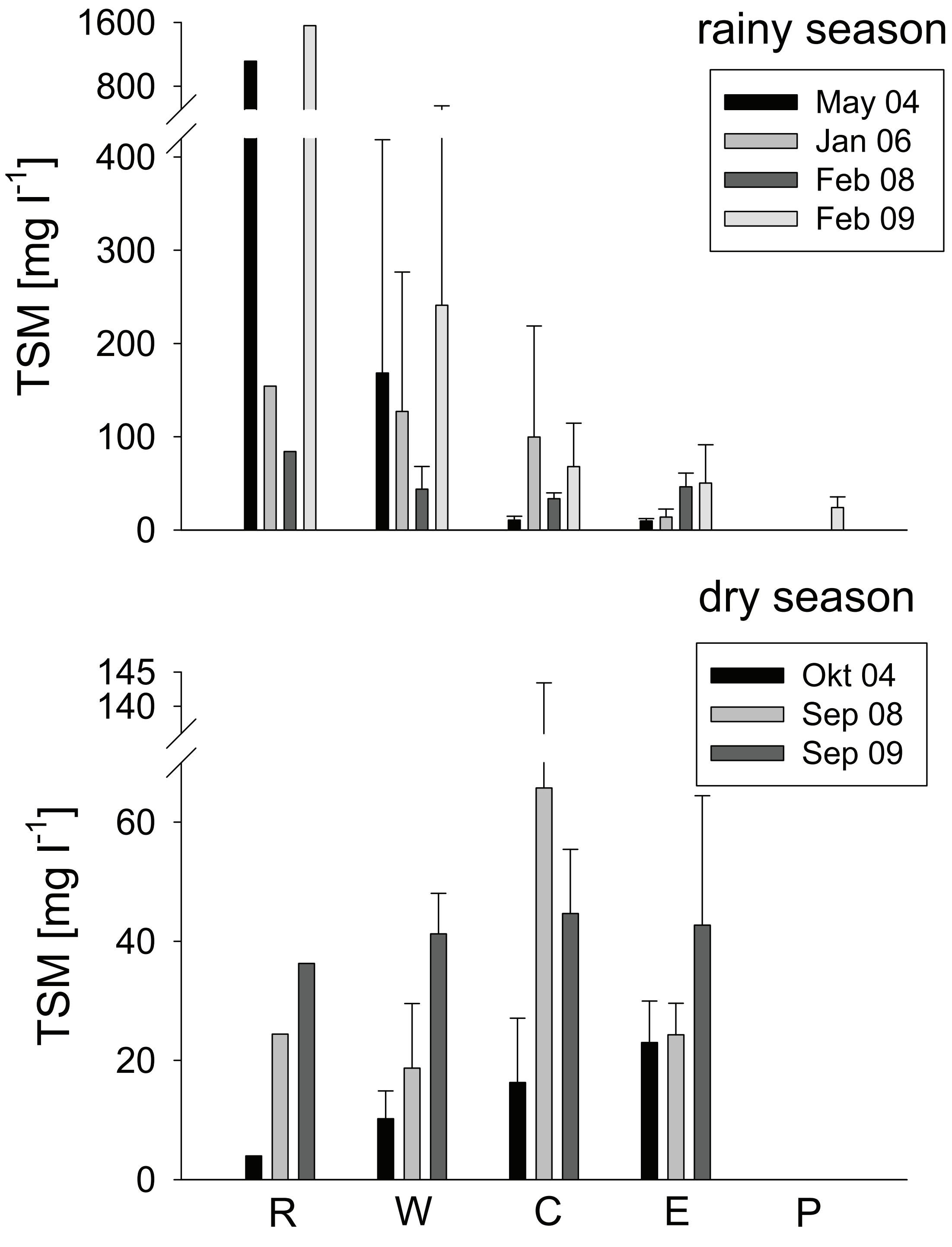

Fig. 2: The total suspended matter load [mg l^{-1}] in the Citanduy and the three lagoon areas during the rainy and the dry season (R= Citanduy River, W= western area, C= central area, E= eastern area, P= Penyu Bay).

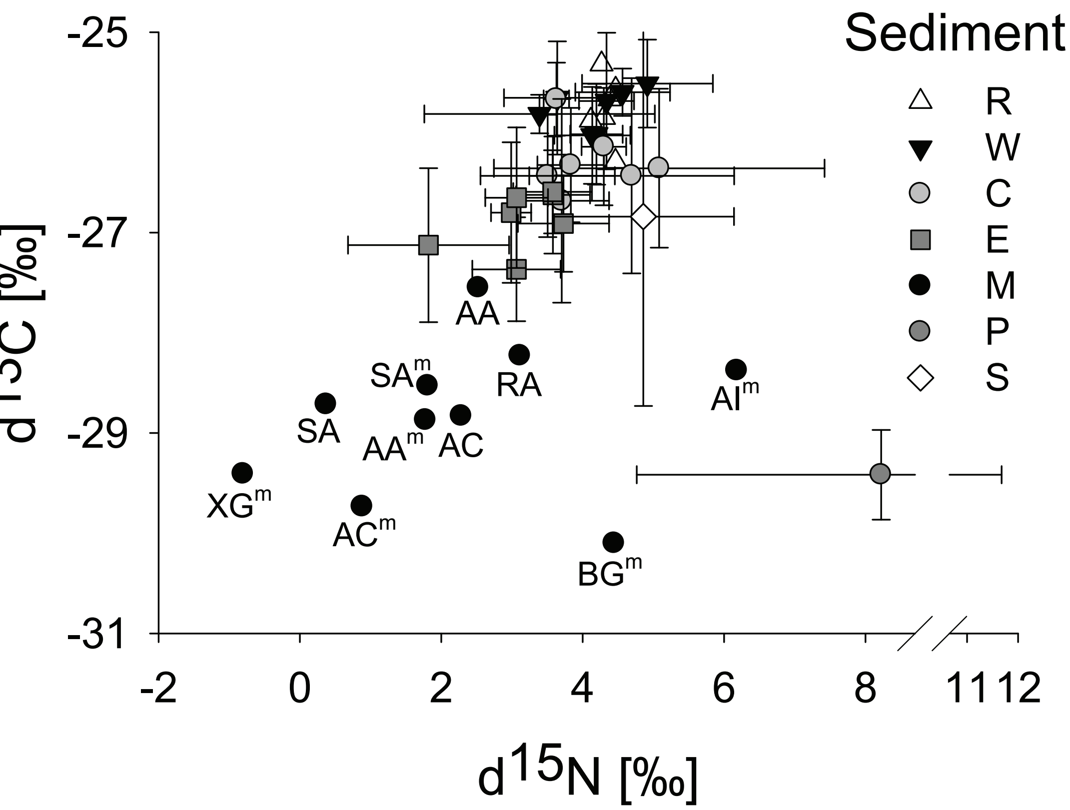

Fig. 3: Stable isotope composition of surface sediments, plants, and soils from the SAL and its hinterland. R= Citanduy River, W= western area, C= central area, E= eastern area, M= brown mangrove leaves (Herbon et al., submitted); P= rice plants (average of grains, leaves, stems and roots); S= soils from rice fields (AA: *Avicennia alba*, AC: *Aegiceras corniculatum*, AI: *Acanthus ilicifolius*, BG: *Bruguiera gymnorrhiza*, RA: *Rhizophora apiculata*, SA: *Sonneratia alba*, XG: *Xylocarpus granatum*). ^{m}= leaves on mud; sampling periods: May 2004, Nov. 2004, Jan. 2006, Sep. 2007, Feb. 2008, Sep. 2008, Feb. 2009 and Sep. 2009).

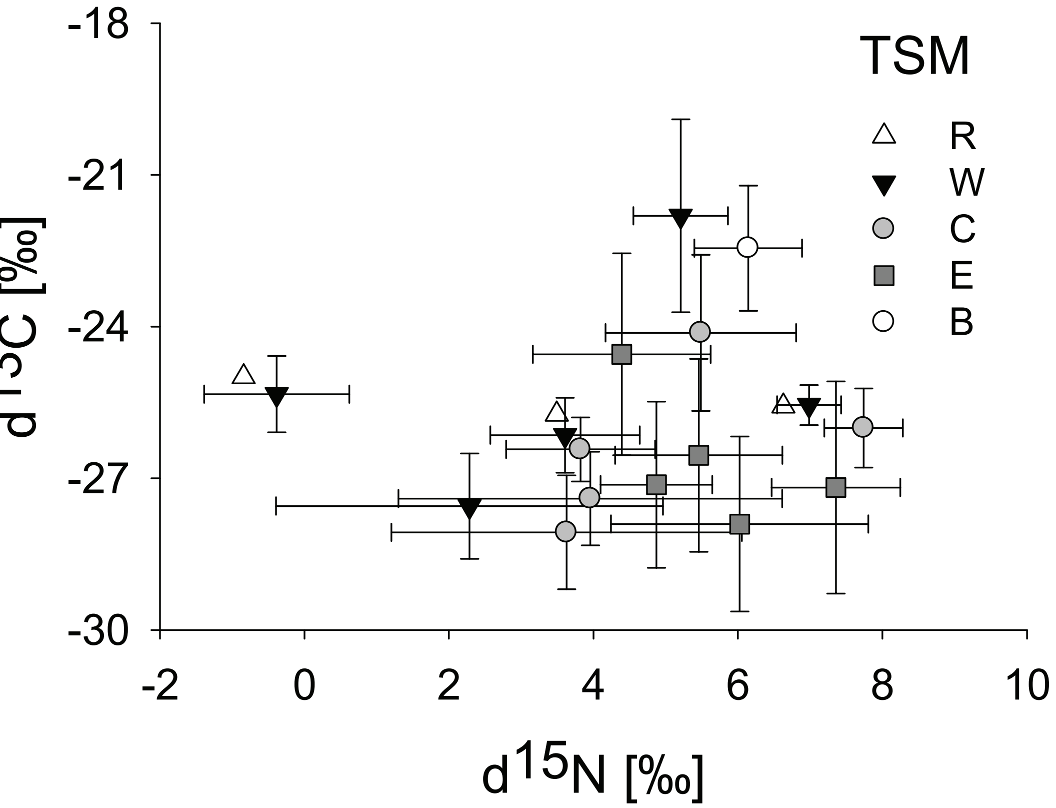

Fig. 4: Stable isotope composition of TSM in SAL and Penyu Bay. R= Citanduy River, W= western area, C= central area, E= eastern area, B= Penyu Bay; sampling periods: May 2004, Nov. 2004, Jan. 2006, Sep. 2007, Feb. 2008, Sep. 2008, Feb. 2009 and Sep. 2009.

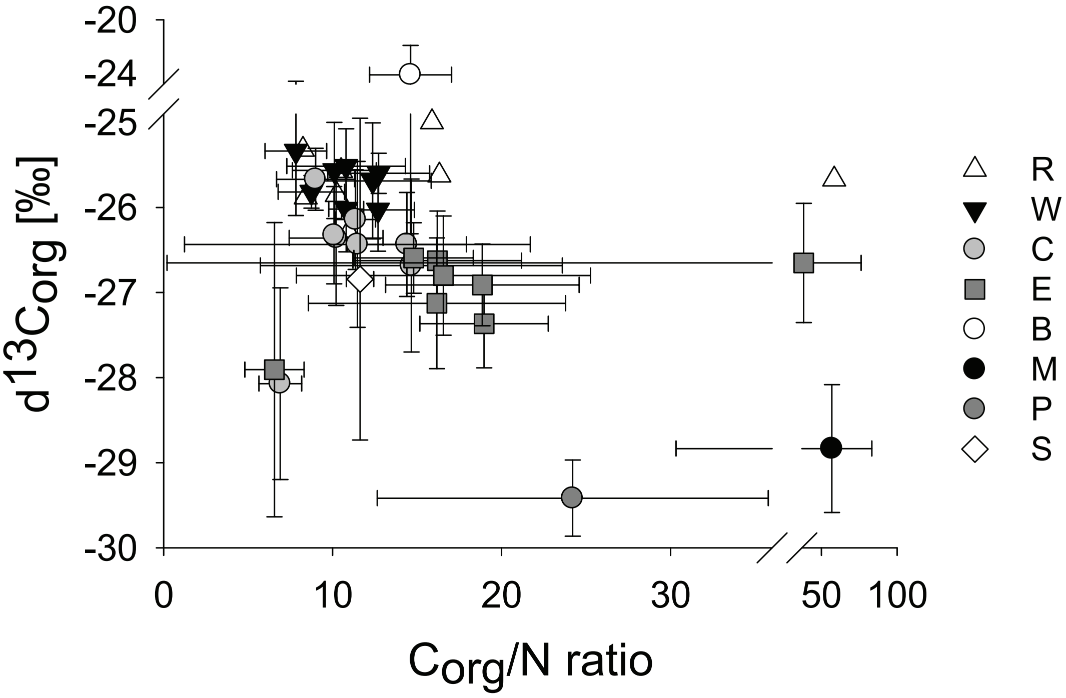

Fig. 5: The $\delta^{13}C$ isotopic composition of the sediment in the Citanduy, the three lagoon areas and Penyu Bay (R= Citanduy River, W= western area, C= central area, E= eastern area, B= Penyu Bay; M= Mangrove, P= Rice plants, S= Rice soils; sampling periods: May 2004, Nov. 2004, Jan. 2006, Sep. 2007, Feb. 2008, Sep. 2008, Feb. 2009 and Sep. 2009).

Tab. 1: The organic carbon and nitrogen content as well as the Corg/N ratio in the TSM and sediment during the dry (DS) and the rainy (RS) season (dry season: average of Nov. 2004, Sep. 2007, Sep. 2008 and Sep. 2009; rainy season: average of Jan. 2005, Feb. 2008 and Feb. 2009).

		Sediment		TSM	
		RS	DS	RS	DS
R	Corg [%]	0.13 ± 0.06	1.11 ± 0.37	1.31 ± 0.15	1.27 ± 0.95
	N [%]	0.01 ± 0.01	0.08 ± 0.05	0.15 ± 0.06	0.11 ± 0.11
	Corg/N	12.4 ± 5.6	22.5 ± 23.9	7.2 ± 0.6	13.7 ± 4.6
W	Corg [%]	0.69 ± 0.41	0.86 ± 0.22	1.53 ± 0.14	1.17 ± 0.79
	N [%]	0.06 ± 0.03	0.07 ± 0.03	0.20 ± 0.03	0.13 ± 0.10
	Corg/N	12.5 ± 0.3	23.4 ± 16.2	7.5 ± 1.0	8.9 ± 2.0
C	Corg [%]	1.19 ± 0.20	1.02 ± 0.22	1.95 ± 0.46	1.66 ± 1.19
	N [%]	0.10 ± 0.01	0.11 ± 0.01	0.25 ± 0.07	0.24 ± 0.19
	Corg/N	12.3 ± 3.0	11.3 ± 2.5	8.2 ± 1.0	7.5 ± 0.5
E	Corg [%]	1.46 ± 0.17	1.51 ± 0.24	2.88 ± 1.65	2.23 ± 2.17
	N [%]	0.09 ± 0.01	0.09 ± 0.01	0.37 ± 0.24	0.32 ± 0.35
	Corg/N	16.8 ± 2.9	22.5 ± 10.6	8.5 ± 1.1	8.6 ± 1.9

Tab. 2: The total hydrolysable amino acid and total hydrolysable hexosamine concentrations [mg g^{-1} and mol%], the contribution of the THAA to the carbon and nitrogen content as well as the Reactivity Index (RI) of the TSM and sediment surface in the Citanduy River and the three lagoon areas during two sampling campaigns (R= Citanduy River, W= western area, C= central area, E= eastern area).

			R	W	C	E
TSM	Feb 09	THAA [mg g^{-1}]	-	6.7 ± 4.6	6.3 ± 6.5	10.7 ± 6.5
		THHA [mg g^{-1}]	-	1.0 ± 0.7	0.8 ± 0.3	1.0 ± 0.5
		THAA-mol%	-	132.6 ± 23.6	126.5 ± 23.7	125.8 ± 23.7
		THHA-mol%	-	16.7 ± 3.8	12.2 ± 2.9	8.3 ± 1.5
		THAA-C%	-	17.4 ± 11.3	17.9 ± 8.7	24.4 ± 9.4
		THAA-N%	-	39.1 ± 25.3	48.5 ± 30.6	51.6 ± 11.1
		RI	-	2.33	2.42	3.14
	Sep 09	THAA [mg g^{-1}]	12.9	10.3 ± 1.9	9.5 ± 4.9	9.3 ± 3.6
		THHA [mg g^{-1}]	1.1	0.8 ± 0.9	0.8 ± 0.4	0.8 ± 0.3
		THAA-mol%	174.7	154.8 ± 16.3	129.7 ± 37.6	128.0 ± 22.2
		THHA-mol%	10.4	8.8 ± 2.2	7.4 ± 2.0	8.4 ± 2.9
		THAA-C%	29.6	26.6 ± 12.2	24.9 ± 4.9	23.8 ± 8.4
		THAA-N%	79.3	74.3 ± 15.5	60.7 ± 15.3	65.8 ± 19
		RI	14.92	6.52	10.03	4.97
Sediment	Feb 09	THAA [mg g^{-1}]	-	-	3.5 ± 1.7	1.9 ± 1.3
		THHA [mg g^{-1}]	-	-	0.7 ± 0.1	0.6 ± 0.7
		THAA-mol%	-	-	85.1 ± 13.4	58.3 ± 26.0
		THHA-mol%	-	-	12.4 ± 3.7	6.9 ± 3.2
		THAA-C%	-	-	9.4 ± 1.4	6.7 ± 1.8
		THAA-N%	-	-	41.5 ± 7.9	37.9 ± 15.6
		RI	-	-	1.68	2.2
	Sep 09	THAA [mg g^{-1}]	0.9	2.3 ± 0.9	2.3 ± 0.2	4.0± 1.8
		THHA [mg g^{-1}]	0.2	0.6 ± 0.3	0.5 ± 0.2	0.8 ± 0.3
		THAA-mol%	92.4	134.2 ± 29.9	124.3 ± 21.8	128.5 ± 36.1
		THHA-mol%	14.6	24.7 ± 7.3	17.3 ± 4.3	17.1 ± 3.7
		THAA-C%	2.5	12.9 ± 2.7	15.7 ± 15.1	14.7 ± 9.5
		THAA-N%	48.1	49.9 ± 7.4	37.9 ± 5.8	44.7 ± 5.1
		RI	1.89	1.73	2.37	2.9

Leaching of dissolved inorganic nutrients from eight mangrove and shrub species in the Segara Anakan Lagoon, Java, Indonesia

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Abstract

Leaching experiments with eight plant species were performed in the mangrove-fringed Segara Anakan Lagoon, Java. The leaching rates of dissolved inorganic nitrogen (DIN), phosphate and silicate were determined at salinity concentrations of 0, 10, 20 and 30 g l^{-1} over a period of 30 days for *Acanthus ilicifolius, Aegiceras corniculatum, Avicennia marina, Bruguiera gymnorrhiza, Ceriops tagal, Derris trifoliata, Rhizophora apiculata* and *Sonneratia caseolaris*. Statistically significant differences between the four salinities were found for DIN and silicate but nor for phosphate. Highest DIN concentrations were measured for *D. trifoliata* with up to 77.2 µM g^{-1} dry weight (dw) followed by *A. ilicifolius* with up to 64.7 µM g^{-1} dw and they were lowest for *B. gymnorrhiza* with up to 3.5 µM g^{-1} dw. Phosphate leaching was highest for *A. marina* with up to 6.5 µM g^{-1} dw whereas highest silicate concentrations were found for *A. ilicifolius* with up to 1808.7 µm g^{-1} dw. A decrease in the nutrient concentrations for all species except for *B. gymnorrhiza* was observed between three to 15 days of the experiment. Large species-specific variations occurred and leaching

concentrations differed by more than one order of magnitude. The vegetation in the SAL changed within the last 25 years due to intensive mangrove tree logging so that nowadays the shrub species *A. ilicifolius* and *D. trifoliata* dominate the plant community in most areas. It is conceivable that the logging-induced shift in vegetation from true mangrove to shrub species will increase the nutrient recycling in the lagoon.

Keywords

Mangrove leaves, leaching, inorganic nutrients, nitrogen, phosphate, silicate, Segara Anakan Lagoon

1. Introduction

Mangroves occur in the tropics and subtropics and connect terrestrial with marine habitats (Day et al. 1987, FAO 2007, Alongi 2008). Its plant litter comprises ~30 to 60% of the total production (Duarte & Cebrián 1996). Typical global average litter fall rates are in the order of ~38 mol C m^{-2} yr^{-1} (Jennerjahn & Ittekkot 2002). Due to outwelling about 50% of the produced litter is transported to adjacent coastal waters (Robertson et al. 1992, Duarte & Cebrián 1996, Dittmar & Lara 2001, Jennerjahn & Ittekkot 2002) where it can serve as the basis for food webs (Odum & Heald 1975, Rodelli et al. 1984, Alongi et al. 1989).

Mangroves need a sufficient supply of nutrients, especially nitrogen and phosphate. However, nutrient concentrations in mangrove waters are low (Alongi et al. 1992, Hogarth 2007, Moll et al. submitted). As the supply of nutrients in mangroves is not sufficient to maintain a high primary production recycling processes are important. Nutrients can derive from rivers and adjacent ecosystems, they can be adsorbed to particles, microorganisms can fix atmospheric nitrogen (Day et al. 1987, Wafar et al. 1997, Machiwa 1999) or they can be brought back into the water column by leaf leaching after litterfall (Stewart & Davies 1989). Leaching of water-soluble compounds, which accounts for a loss of 30 to 50% of the leaf organic matter, is known to be the first step during plant litter degradation (Cundell et al. 1979, Newell et al. 1984, Robertson 1988, Chale 1993, Davis III et al. 2003). The leaf material lost by leaching can vary between species as shown in a leaching study on dissolved organic carbon (DOC) of eight mangrove species where the weight loss ranged between 11 and 65% after 30 d of incubation (Moll et al. submitted). Leaching lasts from a few days to a few weeks (Cundell et al. 1979, Camilleri & Ribi 1986, Steinke et al. 1993, Davis III et al. 2003). Former studies have shown an impact of salt ions on the leaching process like studies on hickory and maple (Lush & Hynes 1973) or on *Avicennia marina* (Steinke et al. 1993) while our study on DOC leaching from mangrove leaves displayed only little influence of salinity (Moll et al. submitted).

Most studies on leaf decomposition used the litter bag technique (Newell et al. 1984, Van der Valk & Attiwill 1984, Robertson 1986, Twilley et al. 1986, Mackey & Smail 1996, Wafar et al. 1997). However, only a few studies dealt with the soluble compounds leached out of leaves. In particular, information on nutrient leaching is rare. Here, we present the results of a leaf leaching experiment and provide information on the inorganic nutrients leached out of leaves from eight abundant mangrove and shrub species in the Segara Anakan Lagoon (SAL). Additionally, the influence of salinity on the leaching process was investigated.

We hypothesize a) that the salinity has a significant effect on the concentration and leaching rate of nutrients from the leaves and b) that the nutrient concentrations leached from leaves differ between species.

2. Material and Methods

2.1 Study area

The SAL (108°46′E – 109°03′E, 7°35′S – 7°48′S; Fig. 1) with an area of 120 km^2 is the largest remaining mangrove stand on the south coast of Java with >9000 ha in 2006 (Ardli & Wolff 2009). The lagoon exchanges water with the Indian Ocean through the western and the eastern outlet. Additionally, the hydrology of the lagoon is governed by the seasonally varying river discharge of the Citanduy River in the western area of the lagoon (White et al. 1989, Yuwono et al. 2007, Holtermann et al. 2009). The different water influences as well as precipitation and evaporation are responsible for varying salinities. Mean salinity is 31 during dry season and 14 during the rainy season with lower values in the western area.

Insert Fig. 1

In the SAL 21 mangrove tree species and five understorey genera occur with tree densities of 0.80 (± 0.99) Ind. m^{-2} (White et al. 1989, Hinrichs et al. 2008). The tree density of true mangrove species is highest for *Aegiceras corniculatum* (28.4%), followed by *Nypa fructicans, Rhizophora apiculata, Ceriops tagal, Sonneratia caseolaris, Bruguiera gymnorrhiza* and *Avicennia marina*. An area of ~37% are covered by shrub species like *Acanthus ilicifolius* and *Derris trifoliata* (Hinrichs et al. 2008). These two species generally occur in mangrove ecosystems with natural and human disturbances since gaps, e.g. due to logging, are rapidly occupied by them (Hogarth 2007). As these two species prefer habitats of low salinity (Joshi & Ghose 2003, Ye et al. 2005) they have higher abundances in the central than in the western part of the lagoon (White et al. 1989).

2.2 Experimental design

A leaf leaching experiment was conducted with leaves from the six mangrove species *Aegiceras corniculatum, Avicennia marina, Bruguiera gymnorrhiza, Ceriops tagal, Rhizophora apiculata* and *Sonneratia caseolaris* as well as with leaves from the shrub species

Acanthus ilicifolius and *Derris trifoliata*. Yellow senescent leaves were hand-picked from the plants. The leaves collected were symmetrical and without damages, except for *A. marina* leaves which often had insect grub areas.

Each leaf was weighed and then submerged in glasses containing 400 ml of artificial sea water at the four salinities 0, 10, 20 and 30 g l^{-1}. Leaves were removed from the glasses at eight times (10 sec, 2 h, 6 h, 1 d, 3 d, 7 d, 15 d and 30 d). For each experimental approach three replicates were prepared. After removing the leaf the water was stirred and 20 ml of the water was filtered through syringe filters (pore size 0.45 µm) and preserved with 4% $HgCl_2$. Samples were stored cool and dark until analysis. Nitrate, nitrite, ammonium, phosphate and silicate concentrations were measured in a Skalar Analytical continuous flow analyzer (determination limits: nitrate: 0.04 µM, nitrite: 0.05 µM, ammonium: 0.06 µM, phosphate: 0.06 µM and silicate: 0.19 µM; coefficient of determination: <3.4%) and detected spectrophotometrically as a coloured complex (Grasshoff & Koroleff 1996). The removed leaf was dried at 40°C and weighed again.

To test if the measured silicate concentrations were influenced by the use of glass three replicates with water at four salinities were set up. The concentrations were subtracted from the leaf leaching data. However, the identical glasses used in the leaf experiment were not available so that similar ones had to be taken instead. The measured concentrations might therefore not represent the true leaching concentrations as using glass is not appropriate for silicate measurements. Nevertheless, we decided to present these data as they can provide information on large differences between species.

2.3 Data analysis and calculations

The nutrient concentration was calculated in µM g^{-1} dry weight (dw). Differences between the four salinities, sampling times and species were tested with a three-way ANOVA using

STATISTICA 9. Due to the standard deviations the p-values were simulated after Westfall and Young (1993).

3. Results

The DIN concentration was highest for *Derris trifoliata* (77.2 ± 20.0 $\mu M\ g^{-1}$ dw after 15 d at 30 $g\ l^{-1}$), *Acanthus ilicifolius* (64.7 ± 62.3 $\mu M\ g^{-1}$ dw after 15 d at 20 $g\ l^{-1}$) and *Ceriops tagal* (47.9 ± 35.3 $\mu M\ g^{-1}$ dw after 15 d at 30 $g\ l^{-1}$). Significantly lower values were found for *Bruguiera gymnorrhiza* with a maximum concentration of 3.5 ± 0.9 $\mu M\ g^{-1}$ dw after 6 h at 20 $g\ l^{-1}$ (Fig. 2, Tab. 1). Maximum concentration for most species was found between three and 15 days. Most of the DIN consisted of ammonium, followed by nitrate. Nitrite concentrations were low for all species, being mostly <2 µM.

Insert Fig. 2 & Tab. 1

Salinity had no effect on the leaching concentrations of phosphate. No phosphate data were available for *D. trifoliata*. Highest phosphate concentrations were measured for *A. marina* leaves with 6.5 $\mu M\ g^{-1}$ dw, followed by *A. ilicifolius*, *A. corniculatum*, *S. caseolaris*, *C. tagal, R. apiculata* and *B. gymnorrhiza* (Fig. 3). All species except for *B. gymnorrhiza* showed a decrease in phosphate concentration after three to 15 days.

Insert Fig. 3

A. ilicifolius leached the highest silicate concentrations with up to 1808.7 $\mu M\ g^{-1}$ dw after 7 d at 30 $g\ l^{-1}$, followed by *S. caseolaris* (1142.2 g^{-1} dw after 30 d at 20 $g\ l^{-1}$) and *D. trifoliata* (1126.8 g^{-1} dw after 30 d at 30 $g\ l^{-1}$) whereas lowest concentrations were measured for *B. gymnorrhiza* (29.1 $\mu M\ g^{-1}$ dw after 30 d at 30 $g\ l^{-1}$, Fig. 4). Silicate concentrations increased over time and did not display a maximum concentration before the end of the experiment for most species.

Insert Fig. 4

4. Discussion

4.1 Interspecific variations

The leached DIN concentrations were significantly different between species and salinity concentrations. The higher nitrogen concentrations were measured at lower salinity for *Avicennia marina, Derris trifoliata, Rhizophora apiculata* and *Sonneratia caseolaris*. In contrast, lower DIN concentrations were observed in freshwater for the other species. It has been shown earlier that DOC leaching from dead mangrove leaves is inhibited by the presence of salt ions (Camilleri & Ribi 1986). In contrast, the investigation of DOC leaching from the same species used in the current experiment showed no or only little influence of salt (Moll et al. submitted). Therefore no general statement on the influence of salt can be made as species are affected differently.

Significant interspecific variations were observed in the current experiment. Highest DIN concentrations were measured for *Derris trifoliata* and *Acanthus ilicifolius*. Mangroves can withdraw up to 77% of nitrogen and 57% of phosphate from their leaves to store these nutrients in other parts of the plant and to use them further (Lin & Wang 2001, Wang et al. 2003). Translocation of nutrients out of senescing leaves back into shoots can be an important nutrient-conservation mechanisms for N and P to maintain growth in nutrient-poor sites (Wang et al. 2003). *Acanthus* and *Derris* are no true mangrove tree but shrub species. They both invaded the SAL within the last 25 years. Both species are abundant in the central area (Hinrichs et al. 2009). There, the lagoon is mainly influenced by the nutrient input of the Citanduy River (Jennerjahn et al. 2009, Moll et al. submitted). This could explain why more nutrients are leached from these two shrub species and might indicate that withdrawing of nutrients might not be necessary. *A. marina* released only little amounts of DIN in the current study. However, it has been shown that this species decomposes faster compared to other species (Wafar et al. 1997).

B. gymnorrhiza had lower nitrogen, phosphate and silicate concentrations. This species is very effective in nutrient resorption as it is able to reduce the initial nitrogen concentration in senescent leaves by up to ~80% (Lin & Wang 2001). *B. gymnorrhiza* occurs mainly in the eastern lagoon (Hinrichs et al. 2009) which is oligotrophic (Jennerjahn et al. 2009). Therefore, the storage of nutrients in other plant parts might be necessary. The DIN leached out of *D. trifoliata* was ~22 times higher than that of *B. gymnorrhiza*. Silicate concentrations also displayed large interspecific variations. Our results indicate internal silicate storage for most species. It has been shown that in senescent leaves of *Sieglingia decumbens* (Heath grass) the silicate deposit is higher than in younger leaves (Sangster 1969). From these observations we assume that mangroves store silicate, possibly in the form of phytoliths, which dissolve and can be released into the water.

The importance of internal nutrient recycling may vary between species. Interspecific differences can be due to different internal nutrient concentrations of leaves and the amount of soluble components (Gosz et al. 1973, Lush & Hynes 1973, Aerts & Caluwe 1997). Our results show high variation among species which might be due to different initial leaf compositions, different nutrient translocation efficiencies and, for some species, different salt concentrations.

4.2 Possible sinks for leached nutrients in the Segara Anakan Lagoon

Most DIN and phosphate concentrations showed a decrease between three and 15 days. The high DIN concentrations in the current study, which consisted mainly of ammonium, can be both explained by a high leaching rate of ammonium as well as by a conversion of nitrate into ammonium by microorganisms. The decrease in DIN concentration is due to uptake by microorganisms to cover their own nutrient supply (Odum et al. 1979, He et al. 1988, Alongi 1994). On all tree parts of mangroves high numbers of bacteria and fungi can be found, e.g. on *Avicennia* and *Rhizophora* 28 higher marine fungi were detected (Kohlmeyer 1969). In an artificial stream the bacteria abundance increased when leaching products of pignut hickory and silver maple was added (Cummins et al. 1972). Nutrient utilization by microorganisms is essential for tropical food webs as nutrient concentrations can be low in mangroves (Alongi et al. 1992, Alongi 1994). Microorganisms in tropical ecosystems are highly productive and efficient in nutrient recycling (Alongi et al. 1989, Alongi et al. 1992).

The concentrations leached out of leaves were much higher than the nutrient concentrations in the SAL reported in earlier studies (Yuwono et al. 2007, Jennerjahn et al. 2009, Moll et al. submitted). The leached concentrations are diluted by oceanic water and can get exported to the ocean. The residence time of the water is between three and nine days in the central lagoon during the rainy season and up to 15 days during the dry season (Holtermann et al. 2009). The leaves can be exported by the tides before the leaching concentrations reach their maximum. In addition, the leached nutrients can immediately be taken up by microorganisms, phytoplankton and phytobenthos as well as by mangrove trees (Bouillon et al. 2008, Kristensen et al. 2008, Jennerjahn et al. 2009). Leached substances can be reabsorbed directly by the roots which improves the growth rate at nutrient-poor sites (Tuckey 1970, Davis III et al. 2003). A nutrient uptake by phytoplankton and phytobenthos seems to be a minor sink in the SAL as the chlorophyll a concentrations in the water column and on the sediment surface were low with 0.1 – 4 $\mu g\ l^{-1}$ (Moll et al. submitted). Even though it is unclear how much of these nutrients are exported or used, it can be concluded that the leaf leaching has a high impact on the nutrient inventory of the lagoon. Possible sinks for nutrients are an uptake by microbes, export to the ocean or consumption by crabs before leaching can reach its maximum.

4.3 Implications for ecology of the Segara Anakan Lagoon

Derris trifoliata and *Acanthus ilicifolius* leached high amounts of nutrients compared to the other species from the SAL. The abundance of these shrub species increased in the last decades in the SAL as they are able to rapidly invade free areas after logging (Hogarth 2007, Hinrichs et al. 2008). Due to the fast invasion of these two shrub species the dispersal of mangrove tree species is inhibited (Ashton & Macintosh 2002). Tree logging reduces terrestrial leaf input into the lagoon. As leaf fall is high in the tropics but the rate of imported nutrients is low nutrient recycling is important (Wang et al. 2003). A further increase in abundance of *A. ilicifolius* and *D. trifoliata* can influence the nutrient concentration and the nutrient recycling in the SAL within the next years.

The nutrient inventory of the SAL is mainly influenced by the inputs of the agriculture-dominated hinterland (Yuwono et al. 2007, Jennerjahn et al. 2009, Moll et al. submitted). A higher input of nitrogen, e.g. by fertilizers, can lead besides a higher mangrove litter production (McKee 1995) to an increase in the nitrogen content in mangrove leaves (Feller et al. 2003) or can even increase mangrove mortality (Lovelock et al. 2009). However, an increase in phosphate does not have an effect on mangrove leaves (Feller et al. 2003). An influence of the increasing nitrogen content in leaves on the consumption rates by micro- and macroorganisms is not yet known but might have an influence on the whole food web. It has been shown that *Carex* species from nutrient-rich sites had higher decomposition rates than those from nutrient-poor sites. An increase in nitrogen can lead therefore to a faster decomposition of leaves (Gosz et al. 1973, Aerts & Caluwe 1997). However, the nutrient concentration in the SAL is low to moderate on a global scale due to the short residence time of the water, a storage of nutrients in sediments or uptake by plants (Jennerjahn et al. 2009, Moll et al. submitted).

The current study showed large interspecific variations in the leaching concentrations, which differed for some species even by more than one order of magnitude. A vegetation shift in the

SAL within the last 25 years due to intensive mangrove tree logging was observed so that nowadays the shrub *A. ilicifolius* and *D. trifoliata* dominate the plant community in most areas. As these two species displayed the highest leaching rates it is conceivable that the logging-induced shift in vegetation from true mangrove to shrub species can increase the nutrient recycling in the lagoon.

Acknowledgement

We thank Edy Yuwono and Husein Sastranegara for their support, Yuni Yumiarti for helping us in the field, Carolin Herbon, Anne Buhmann, Dana Pargmann and Alexandra Ostmann for their help and Matthias Birkicht for help with laboratory work. Financial support by the German Federal Ministry of Education and Research (Grant No. 03F0471A) within the SPICE (Science for the Protection of Indonesian Coastal Marine Ecosystems) program is gratefully acknowledged. This study was additionally supported by the Bremen International Graduate School for Marine Sciences (GLOMAR) that is funded by the German Research Foundation (DFG).

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Figures and tables

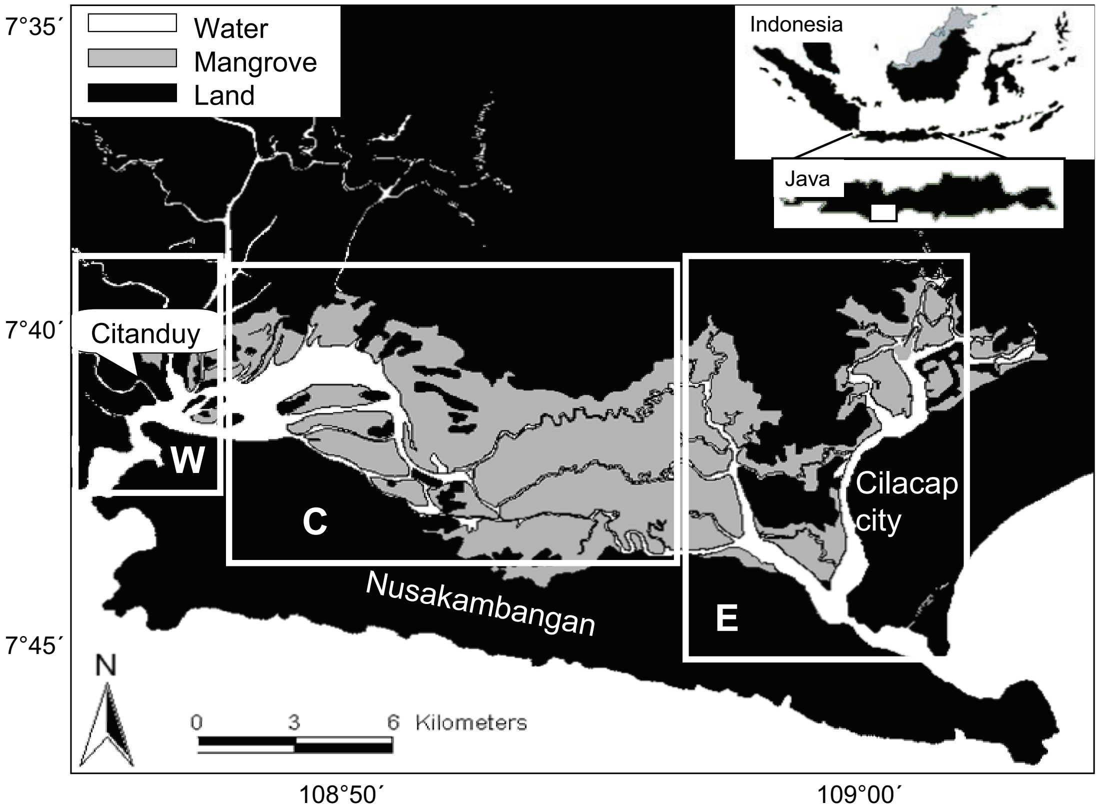

Fig. 1: Map of Segara Anakan including the Citanduy River and the three sampling areas (W= west, C= central, E= east).

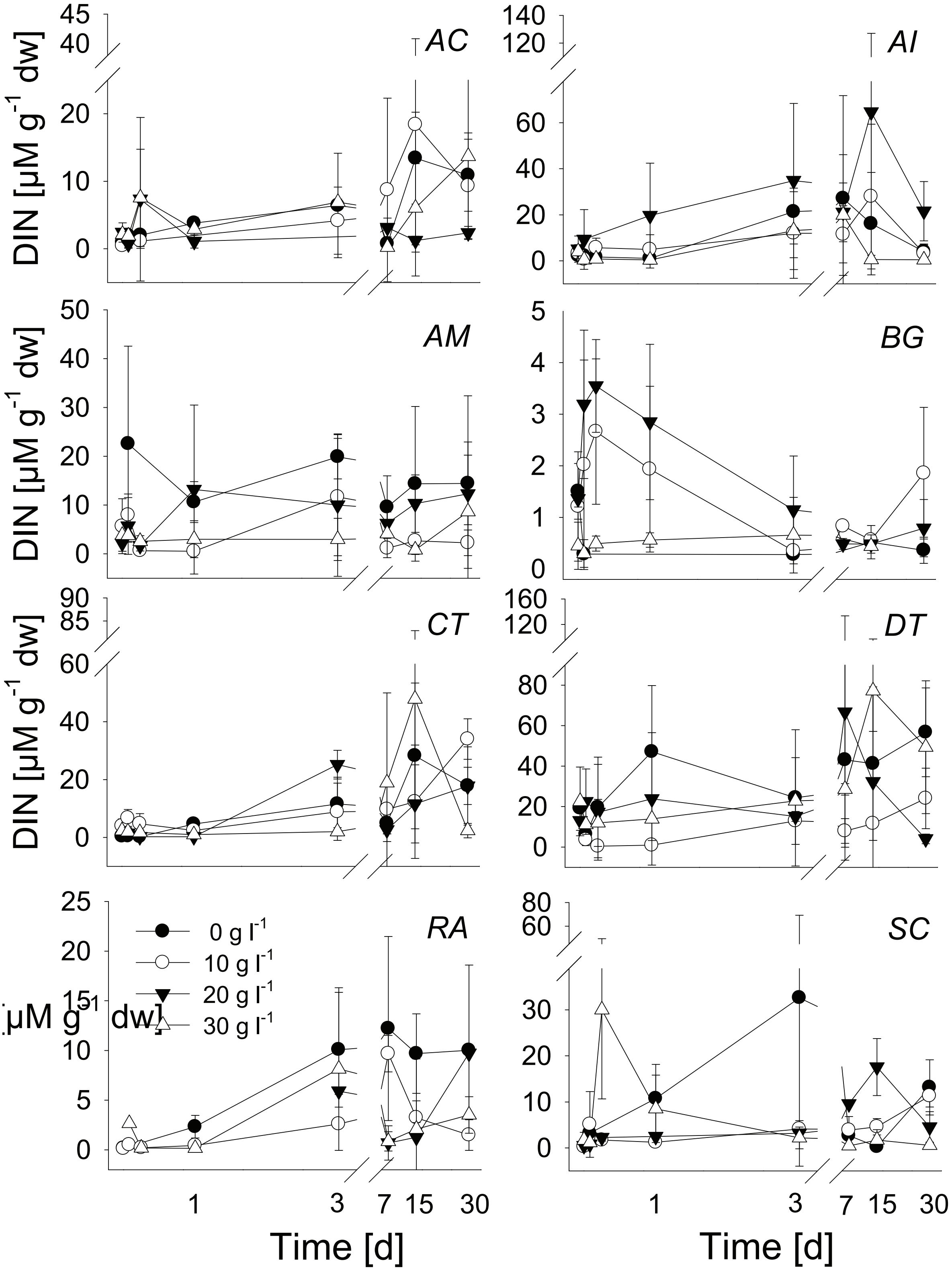

Fig. 2: The leached dissolved inorganic nitrogen concentration (DIN in µM g^{-1} dw ± S.D.) at four salinity concentration (AC= *Aegiceras corniculatum*, AI= *Acanthus ilicifolius,* AM= *Avicennia marina*, BG= *Bruguiera gymnorrhiza*, CT= *Ceriops tagal*, DT= *Derris trifoliata*, RA= *Rhizophora apiculata*, SC= *Sonneratia caseolaris*).

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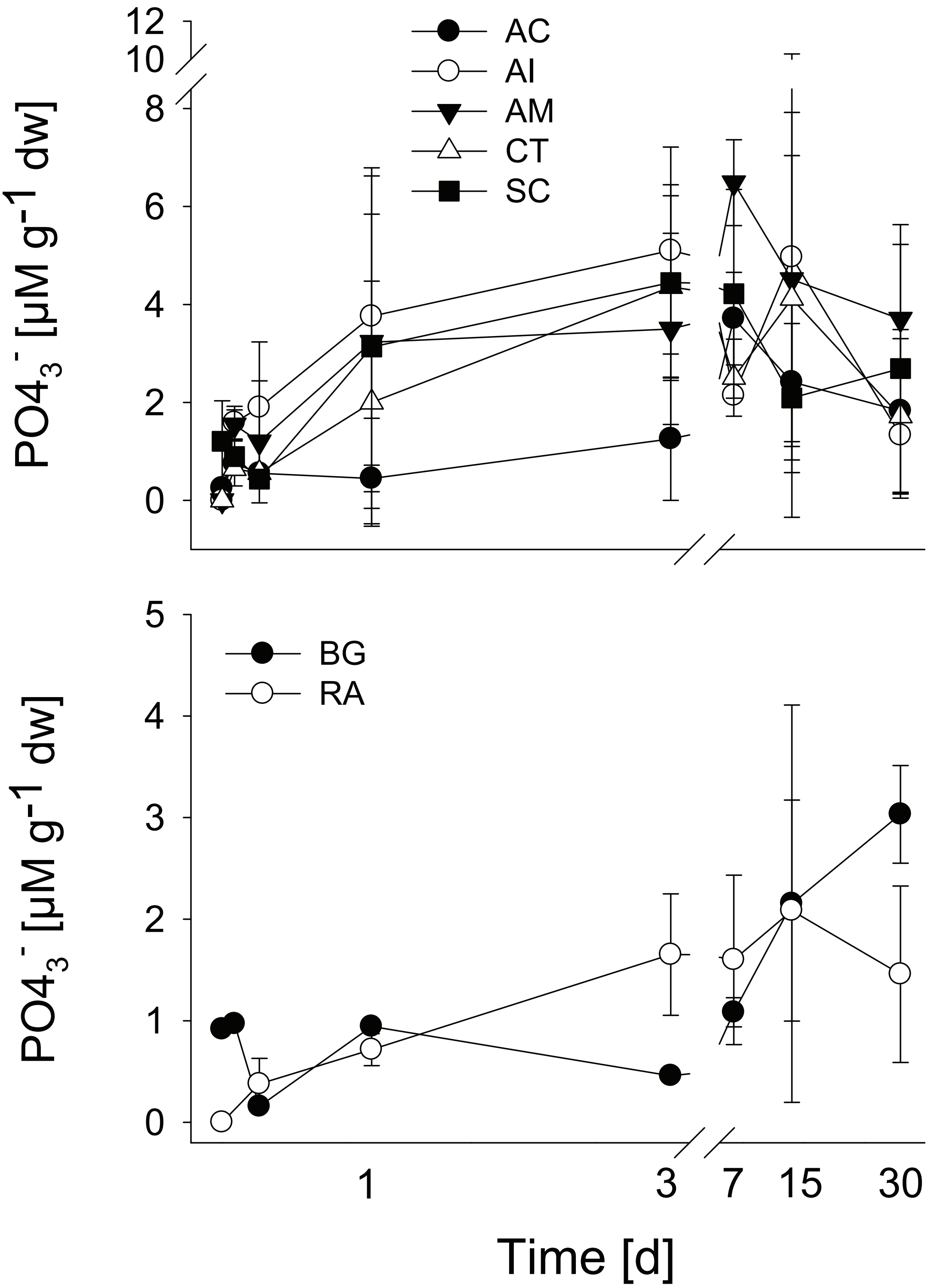

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424 **Fig. 3:** The mean leached phosphate concentrations (PO_4^{3-} in µM g^{-1} dw ± S.D.) for the four salinity approaches,
425 separated for clarity into the lower concentration (lower graph), and the higher concentrations (upper graph).
426 AC= *Aegiceras corniculatum*, AI= *Acanthus ilicifolius,* AM= *Avicennia marina*, BG= *Bruguiera gymnorrhiza*,
427 CT= *Ceriops tagal*, RA= *Rhizophora apiculata*, SC= *Sonneratia caseolaris*.

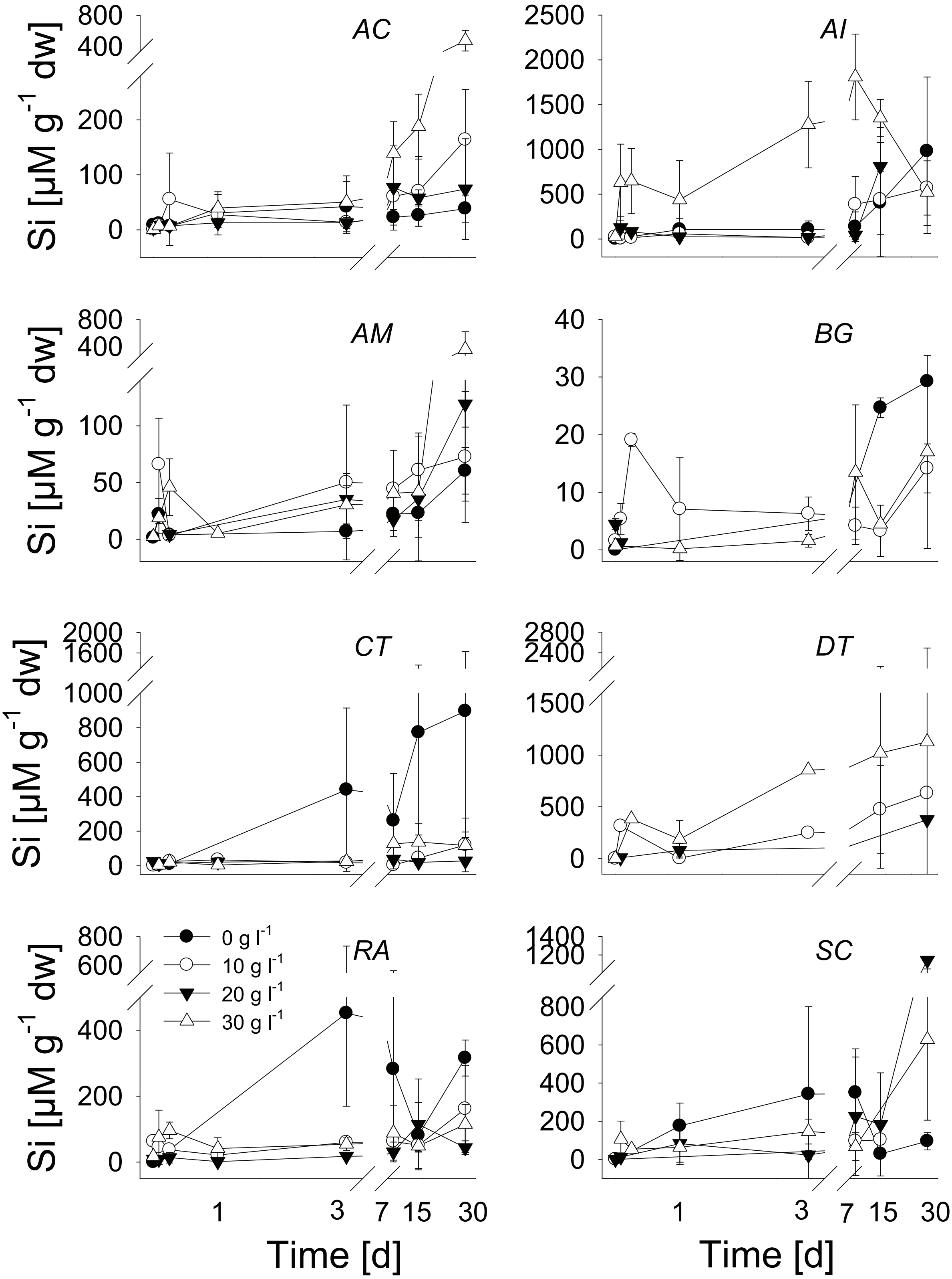

Fig. 4: The leached silicate concentrations (Si in mM g^{-1} dw ± S.D at four salinity concentration (AC= *Aegiceras corniculatum*, AI= *Acanthus ilicifolius,* AM= *Avicennia marina*, BG= *Bruguiera gymnorrhiza*, CT= *Ceriops tagal*, DT= *Derris trifoliata*, RA= *Rhizophora apiculata*, SC= *Sonneratia caseolaris*).

Tab. 1: The interactions between species, time and salinity based on a three-way ANOVA for phosphate, dissolved inorganic nitrogen and silicate (SS= sum of squares, Dgr. F= degree of freedom, MS= Means, F= test statistic of the F-test after Fisher, p= significance level, * significant parameter influencing the leaching rate).

		SS	Dgr F	MS	F	p
PO_4^{3-}	species	152.8	6	25.5	7,20	0,000*
	sal	12.4	3	4.1	1,17	0,398
	time	103.7	7	14.8	4,19	0,002*
	species*sal	117.6	17	6.9	1,95	0,202
	species*time	130.3	36	3.6	1,02	0,555
	sal*time	53.3	19	2.8	0,97	0,429
	species*sal*time	200.2	43	4.7	1,32	0,291
DIN	species	22012.3	7	3144.6	15,96	0,000*
	sal	1831.1	3	610.4	3,10	0,005*
	time	7507.3	7	1072.5	5,44	0,000*
	species*sal	9422.4	21	448.7	2,28	0,021*
	species*time	13306.3	49	271.6	1,38	0,105
	sal*time	1778.5	21	84.7	0,43	0,923
	species*sal*time	26681.6	126	211.8	1,07	0,428
$Si(OH)_4^-$	species	6238708.3	7	891244.0	15,44	0,000*
	sal	1367868.8	3	455956.3	7,9	0,001*
	time	3076228.2	7	439461.2	7,61	0,004*
	species*sal	8333951.5	20	416697.6	7,22	0,001*
	species*time	5010237.1	48	104379.9	1,81	0,234
	sal*time	1089505.6	21	51881.2	0,9	0,298
	species*sal*time	7229679.8	90	80329.8	1,39	0,168